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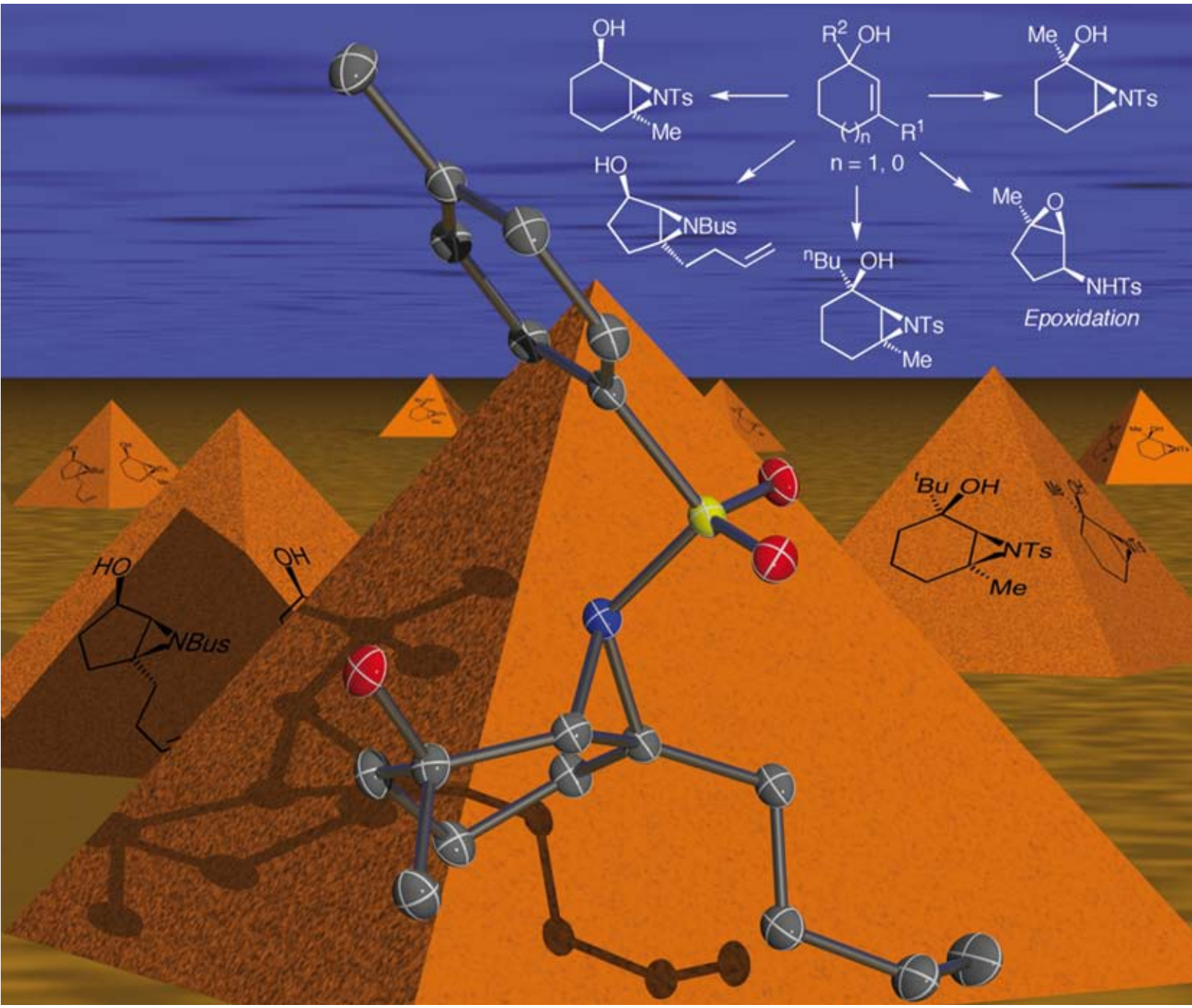

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Stereoselective aziridination of cyclic allylic alcohols using chloramine-T†

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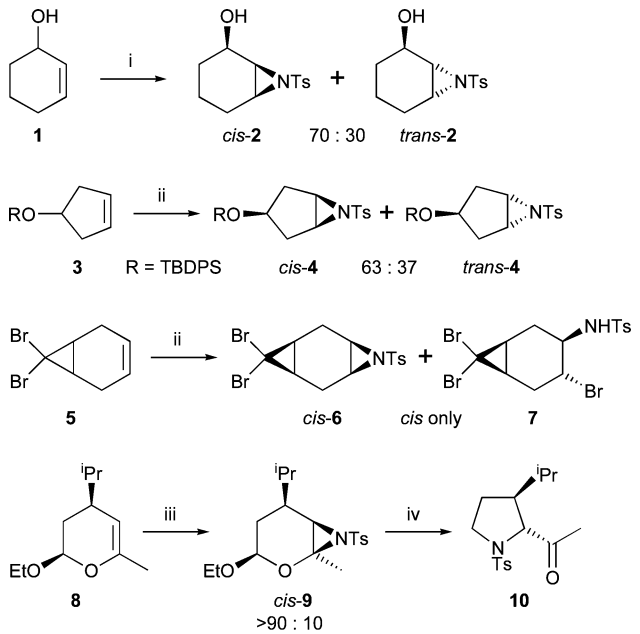
The stereoselective aziridination of a range of cyclic allylic alcohols using two different chloramine salts (4-$MeC_6H_4SO_2NClNa$, TsNClNa and *t*-$BuSO_2NClNa$, BusNClNa) has been explored. The stereoselectivity of these reactions was highly dependent on the structure of the allylic alcohol and the chloramine salt. Generally, mixtures of *cis*- and *trans*-hydroxy aziridines were obtained, in which the major diastereomer was the *cis*-hydroxy aziridine, whilst complete *cis*-diastereoselectivity was observed in the aziridination of 1,3-disubstituted allylic alcohols. In each case studied, aziridination using BusNClNa gave higher *cis*-stereoselectivity than that observed for the same reaction using TsNClNa. Unexpectedly, application of the aziridination conditions to 1-substituted cyclopen-2-en-1-ols did not generate the aziridines. Instead, epoxy sulfonamides were obtained.

Introduction

As part of a programme of research on the organolithium-mediated α-lithiation and further elaboration of *N*-sulfonyl aziridines,[1–5] we required a simple and general method for the direct synthesis of a wide range of aziridines, especially those from cyclic allylic alcohols. In most cases, aziridination was successfully accomplished using Sharpless–Komatsu-type conditions[6,7] (chloramine-T, X^+ source) and we became particularly interested in the factors affecting the diastereoselectivity of aziridination of cyclic allylic alcohols using these conditions. Perhaps surprisingly, there are only a few reports on the diastereoselectivity of alkene aziridination using any reagents. For example, Atkinson and co-workers have described a number of highly stereoselective aziridinations using their *N*-acetoxyquinazolone reagents.[8] In general, steric factors tended to control the stereoselectivity although, for allylic alcohols, Henbest-like[9] *cis*-stereoselectivity was observed using an *N*-acetoxyquinazolone. Similarly, Cu(I) or Cu(II) salts and iodinanes ($PhI{=}NSO_2Ar$) give sterically-controlled aziridinations, as noted by Evans,[10] Hudlicky,[11] Wood[12] and ourselves.[13]

In contrast, since the Sharpless–Komatsu aziridination (TsNClNa, X^+ source) proceeds *via* an intermediate bromonium ion, it generally leads to stereoselectivity that is complementary to the direct sterically-controlled processes. Some examples illustrating this are shown in Scheme 1. Thus, in Sharpless' original disclosure, it was reported that aziridination of cyclic allylic alcohol **1** proceeded to give a 70 : 30 mixture of aziridines *cis*- and *trans*-**2**.[6] In a similar fashion, we reported that aziridination of protected hydroxy cyclopentene **3** gave a 63 : 37 mixture of aziridines *cis*- and *trans*-**4**.[13] Subsequently, O'Doherty and co-workers found that aziridination of cyclopropyl-alkene **5** was completely *cis*-stereoselective giving only *cis*-**6** and amino bromide **7** (which could be cyclised to *cis*-**6** *via* a separate base-mediated step).[14] As a final example, Armstrong *et al.* used Sharpless-like aziridination to convert enol ether **8** into a presumed intermediate aziridine *cis*-**9**, which was eventually rearranged into keto pyrrolidine **10** with *trans*-relative stereochemistry.[15] In all four examples, it can be assumed that preferential bromination *trans* to the substituent occurs leading to *cis*-aziridination after ring-opening by the amino nucleophile (TsNClNa). However, since alkene bromination is likely to be reversible, it may be that faster ring-opening of a *trans*-bromonium ion is responsible for the overall *cis*-stereoselectivity of the aziridination.



Scheme 1 *Reagents and conditions:* i, 1.1 eq. TsNClNa, 0.1 eq. $PhMe_3N^+Br_3^-$, MeCN, rt, 12 h. ii, 1.1 eq. $TsNClNa{\cdot}3H_2O$, 0.1 eq. $PhMe_3N^+Br_3^-$, MeCN, rt, 16 h. iii, 3.0 eq. TsNClNa, 0.2 eq. NBS, MeCN, rt, 1 h. iv, 3 eq. Et_3SiH, 2 eq. $BF_3{\cdot}Et_2O$, −78 °C → 0 °C, 2 h.

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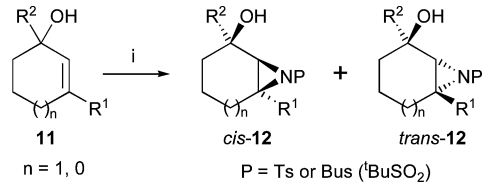
† Electronic supplementary information (ESI) available: Additional experimental procedures (synthesis of allylic alcohols). CCDC reference numbers 692182 (*cis*-**83**) and 692183 (*cis*-**93**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b811137e

‡ Author to whom correspondence regarding the X-ray crystal structure should be addressed.

In this paper, we report a wide range of results on the stereoselective aziridination of cyclic allylic alcohols **11** → *cis*- and *trans*-**12** using Sharpless reaction conditions (Scheme 2). Specifically, we have studied cyclopentene- and cyclohexene-derived allylic alcohols **11** with different substitution patterns (R^1, R^2) as well as the effect of the *N*-sulfonyl part of the aziridinating reagent. In general, moderate to good *cis*-stereoselectivity was observed but we also encountered a number of unexpected results. Herein, we report the full details of our study.

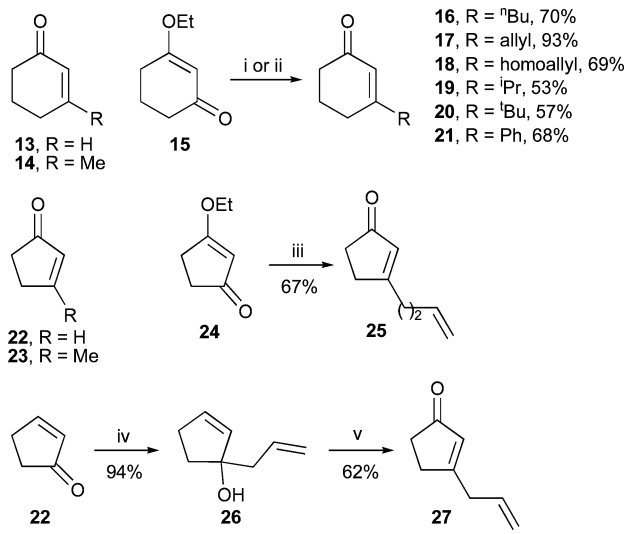


Scheme 2 *Reagents and conditions:* i, 1.1 eq. $TsNClNa{\cdot}3H_2O$ or 1.2 eq. BusClNa, 0.1 eq. $PhMe_3N^+Br_3^-$, MeCN, rt, 12 h.

Results and discussion

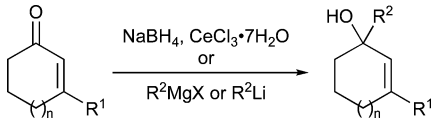
Synthesis of cyclic allylic alcohols

The synthesis of the required cyclopentene- and cyclohexene-derived allylic alcohols was carried out using established routes as shown in Scheme 3 and Table 1. Generally, a two-step route was employed: synthesis of the cyclic enone and subsequent 1,2-reduction or 1,2-addition of an appropriate organometallic reagent. Cyclic enones **13**, **14**, **22** and **23** are commercially available. For the preparation of 3-substituted enones **16–21** and **25**, addition of a Grignard or organolithium reagent to vinyl ether **15** or **24** and subsequent aqueous acidic work-up was utilised (Scheme 3). In contrast, the best way of synthesising allyl-substituted cyclopentenone **27** was *via* 1,2-addition of allyl magnesium bromide to cyclopentenone **22** to give **26** and then PDC-mediated rearrangement.[16] The cyclic allylic alcohols were



Scheme 3 *Reagents and conditions:* i, (a) RLi, Et_2O, –78 °C, 0.5 h; (b) $H_2SO_{4(aq)}$; ii, (a) RMgX, THF, 0 °C, 4 h; (b) $H_2SO_{4(aq)}$; iii, (a) homoallylMgBr, THF, rt, 2 h; (b) $H_2SO_{4(aq)}$; iv, allylMgCl, THF, rt; v, PDC, CH_2Cl_2, rt.

Table 1 Synthesis of allylic alcohols



Entry	*n*	R^1	SM	Reagent[a]	R^2	Product	Yield (%)[b]
1	1	H	**13**	$NaBH_4$	H	**1**	43
2	1	Me	**14**	$NaBH_4$	H	**28**	64
3	1	*n*-Bu	**16**	$NaBH_4$	H	**29**	81
4	1	Allyl	**17**	$NaBH_4$	H	**30**	66
5	1	Homoallyl	**18**	$NaBH_4$	H	**31**	95
6	1	*i*-Pr	**19**	$NaBH_4$	H	**32**	75
7	1	*t*-Bu	**20**	$NaBH_4$	H	**33**	85
8	1	Ph	**21**	$NaBH_4$	H	**34**	79
9	0	H	**22**	$NaBH_4$	H	**35**	36
10	0	Me	**23**	$NaBH_4$	H	**36**	53
11	0	Allyl	**27**	$NaBH_4$	H	**37**	74
12	0	Homoallyl	**25**	$NaBH_4$	H	**38**	80
13	1	H	**13**	R^2MgX	Me	**39**	69
14	1	H	**13**	R^2Li	*n*-Bu	**40**	74
15	1	H	**13**	R^2MgX	Allyl	**41**	64
16	1	H	**13**	R^2Li	*i*-Pr	**42**	64
17	0	H	**22**	R^2MgX	Me	**43**	42
18	0	H	**22**	R^2Li	*n*-Bu	**44**	62
19	1	Me	**14**	R^2Li	Me	**45**	65
20	1	Me	**14**	R^2Li	*n*-Bu	**46**	82
21	1	*n*-Bu	**16**	R^2Li	Me	**47**	68
22	1	Allyl	**17**	R^2Li	*n*-Bu	**48**	70
23	1	*i*-Pr	**19**	R^2Li	*n*-Bu	**49**	87
24	0	Me	**23**	R^2MgX	Me	**50**	44
25	0	Me	**23**	R^2Li	*n*-Bu	**51**	60
26	0	Allyl	**27**	R^2Li	*n*-Bu	**52**	45

[a] *Reaction conditions:* $NaBH_4$: $NaBH_4$, $CeCl_3{\cdot}7H_2O$, MeOH, 0 °C to rt, 0.5 h; R^2MgX: R^2MgX, THF, 0 °C to rt, 12 h; R^2Li: R^2Li, Et_2O, –78 °C, 15 min. Full details of the synthesis of **1** and **28–52** are provided in the ESI.† [b] Yield after distillation or chromatography.

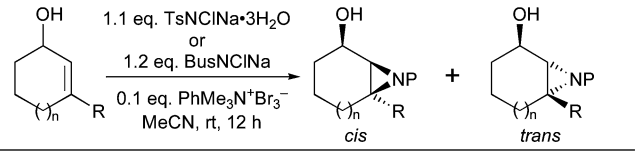
then prepared from the enones by Luche reduction ($NaBH_4$–$CeCl_3{\cdot}7H_2O$) for the 3-substituted allylic alcohols (Table 1, entries 1–12) or by 1,2-addition of the appropriate Grignard or organolithium reagent for the 1-substituted (Table 1, entries 13–18) and 1,3-disubstituted allylic alcohols (Table 1, entries 19–26).

Aziridination of 3-substituted cyclic allylic alcohols

With the cyclic allylic alcohols in hand, we then studied the diastereoselectivity of their aziridination using commercial chloramine-T trihydrate ($TsNClNa{\cdot}3H_2O$) or BusNClNa (Bus = *t*-$BuSO_2$) (prepared according to a literature method[17]) and 0.1 eq. of $PhMe_3N^+Br_3^-$ (source of Br^+) in MeCN at room temperature for typically 12 hours (Sharpless conditions[6]). The diastereoselectivity was determined from the ^1H NMR spectra of the crude products and, where possible, the *cis*- and *trans*-hydroxy aziridines were then separated by chromatography or recrystallisation.

The results of the aziridination of the 3-substituted cyclohex-2-en-1-ols and cyclopent-2-en-1-ols are presented in Table 2. Using $TsNClNa{\cdot}3H_2O$, the reactions were moderately *cis*-diastereoselective (*cis* : *trans* 60 : 40–75 : 25) across most of the allylic alcohols (Table 2, entries 1–5 and 9–12). The lowest degree of stereoselectivity was obtained when R = H (**1** and **35**) (Table 2, entries 1 and 9) or when R = *i*-Pr (**32**) (Table 2, entry 6). Better levels of *cis*-stereoselectivity were obtained with R = Me, *n*-Bu, allyl or homoallyl and this allowed useful yields of pure

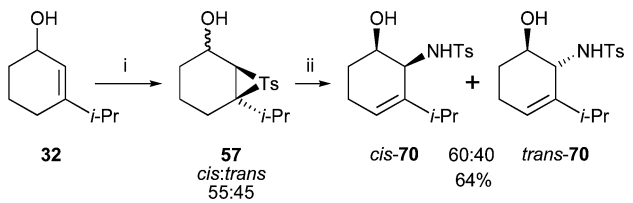
Table 2 Aziridination of 3-substituted cyclic allylic alcohols



Entry	*n*	R	SM	P	Product	*cis* : *trans*[a]	Yield of *cis* (%)[b]	Yield of *trans* (%)[b]
1	1	H	**1**	Ts	**2**	60 : 40	57	25
2	1	Me	**28**	Ts	**53**	75 : 25	68	0[c]
3	1	*n*-Bu	**29**	Ts	**54**	70 : 30	45	13
4	1	Allyl	**30**	Ts	**55**	65 : 35	71[d]	
5	1	Homoallyl	**31**	Ts	**56**	70 : 30	34	12
6	1	*i*-Pr	**32**	Ts	**57**	55 : 45	—[e]	—
7	1	*t*-Bu	**33**	Ts	**58**	—	0	0
8	1	Ph	**34**	Ts	**59**	—[f]	—[g]	—[g]
9	0	H	**35**	Ts	**60**	60 : 40	44	23
10	0	Me	**36**	Ts	**61**	75 : 25	63	12
11	0	Allyl	**37**	Ts	**62**	65 : 35	56	22
12	0	Homoallyl	**38**	Ts	**63**	65 : 35	53	15
13	1	H	**1**	Bus	**64**	70 : 30	34	0[c]
14	1	Me	**28**	Bus	**65**	90 : 10	68	0[c]
15	1	Homoallyl	**31**	Bus	**66**	80 : 20[h]	50	0[c,i]
16	0	H	**35**	Bus	**67**	80 : 20	42	0[c]
17	0	Me	**36**	Bus	**68**	95 : 5	51	0[c,i]
18	0	Homoallyl	**38**	Bus	**69**	—[f,h]	75	0[c,i]

[a] Ratio determined by ^{1}H NMR spectroscopy of the crude product. [b] Yield after chromatography. [c] *trans*-Hydroxy aziridine not isolated after chromatography. [d] *cis*- and *trans*-hydroxy aziridines isolated as a mixture. [e] *cis*- and *trans*-**57** underwent rearrangement upon chromatography on silica (see Scheme 4). [f] Ratio could not be determined. [g] *cis*- and *trans*-**59** could not be separated from other by-products. [h] Reaction carried out in acetone. [i] Purified by chromatography and recrystallisation.

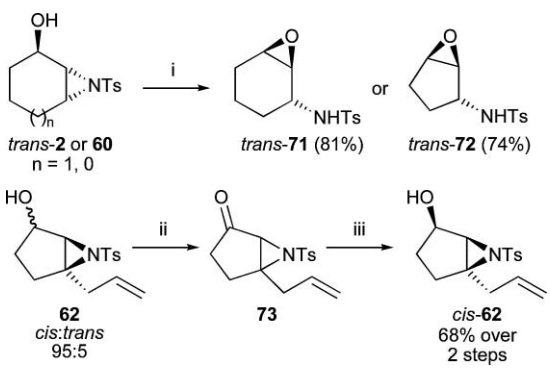
cis-diastereomers to be isolated from these reactions. Interestingly, there was no evidence of terminal alkene aziridination from the ^{1}H NMR spectra of the crude products of any of the reactions with allyl or homoallyl-substituted allylic alcohols. Apparently, there is good regiocontrol and the adjacent hydroxyl group provides a directing effect for the aziridination under these conditions. We identified three troublesome allylic alcohols. With the most sterically hindered allylic alcohol **33** (R = *t*-Bu), a complex mixture of products was obtained, none of which appeared to be aziridines. Similarly, with allylic alcohol **34** (R = Ph), only small quantities of aziridines were formed and they could not be separated from other unidentified by-products. Finally, with allylic alcohol **32** (R = *i*-Pr), a 55 : 45 mixture of aziridines *cis*- and *trans*-**57** was formed in the crude product mixture (as judged by ^{1}H NMR spectroscopy). However, upon purification by chromatography on silica, *cis*- and *trans*-**57** rearranged to give a 60 : 40 mixture of hydroxy sulfonamides *cis*- and *trans*-**70** in 64% yield (Scheme 4).



Scheme 4 *Reagents and conditions:* i, 1.1 eq. TsNClNa·3H$_2$O, 0.1 eq. PhMe$_3$N$^+$Br$_3^-$, MeCN, rt, 12 h; ii, silica gel.

Six allylic alcohols (**1**, **28**, **31**, **35**, **36** and **38**) were also aziridinated using BusNClNa for comparison (Table 2, entries 13–18). The BusNClNa reactions were generally lower yielding but proceeded with higher stereoselectivity than their TsNClNa·3H$_2$O counterparts (Table 2, compare entries 1 and 13). Indeed, the highest levels of *cis*-stereoselectivity (90 : 10–95 : 5) were observed using BusNClNa (Table 2, entries 14 and 17). Unfortunately, BusNClNa is not commercially available[18] (unlike TsNClNa·3H$_2$O) and the yields were generally lower compared to TsNClNa·3H$_2$O.

The relative stereochemistry of all of the *cis*- and *trans*-hydroxy aziridines shown in Table 2 was established by a combination of methods. First, four of the *trans*-hydroxy aziridines (**2**, **56**, **60** and **62**) were subjected to aza-Payne rearrangement[19] to the corresponding *trans*-epoxides. Two examples are shown in Scheme 5. Thus, treatment of hydroxy aziridine *trans*-**2** with KHMDS in THF at 0 °C led to smooth conversion into *trans*-**71**, a known[20] compound, that was isolated in 81% yield. Similarly, hydroxy aziridine *trans*-**60** gave epoxide *trans*-**72** (74% yield). Only the *trans*-hydroxy aziridines can undergo such a reaction. Next, seven of the *cis*-hydroxy aziridines (**2**, **53**, **55**, **56** and **60–62**) were prepared independently by reduction of their corresponding keto aziridines. By analogy with the reduction of related keto aziridines[21] and epoxides,[22] *anti*-addition of hydride to the keto aziridines can be envisaged to occur (attack on the *exo*-face of the keto aziridine and *anti* to the C–N bond). As a representative example, oxidation of hydroxy aziridines **62** gave keto aziridine **73**, which was reduced with NaBH$_4$ to hydroxy aziridine *cis*-**62** in 68% yield over the two steps, with no evidence for the formation of any *trans*-**62** (Scheme 5). Finally, using the above unequivocally assigned examples, we have noted some useful diagnostic trends in the ^{1}H NMR spectra of the *cis*- and *trans*-hydroxy aziridines. Thus, the CHN signals in the *cis*-hydroxy aziridines show a vicinal coupling constant (to the adjacent CHO proton), $^3J = 2.0$–5.0 Hz. In contrast, the CHN signals in the *trans*-hydroxy aziridines show $^3J = 0$ Hz *i.e.* the CHN proton does not couple to the CHO proton and the dihedral angle must therefore be essentially 90°. In addition, in each pair of diastereomers, the CHN signal for the *cis*-hydroxy aziridine appears downfield of the signal for the corresponding *trans*-hydroxy aziridine. These trends in the ^{1}H NMR spectroscopic data are summarised in Fig. 1 and are also consistent with Atkinson's stereochemical assignments of related hydroxy aziridines.[23]



Scheme 5 *Reagents and conditions:* i, 4 eq. KHMDS, THF, 0 °C, 3 h. ii, Dess–Martin periodinane, CH_2Cl_2, rt, 2 h. iii, $NaBH_4$, MeOH, 0 °C, 3 h.

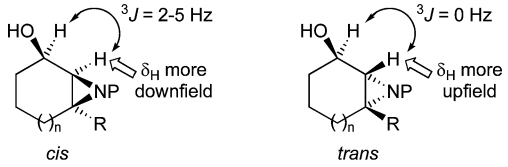


Fig. 1 Diagnostic trends in ^{1}H NMR spectroscopic data for *cis* and *trans* hydroxy aziridines.

The higher stereoselectivity observed using BusNClNa compared to that obtained with TsNClNa deserves further comment and discussion. In particular, different levels of stereoselectivity are observed using both reagents for the *same* allylic alcohol. Thus, it can be concluded that bromonium ion formation is reversible and the diastereoselectivity arises from different rates of attack on the bromonium ions (*e.g. cis*-**74** and *trans*-**74**) by the TsNClNa or BusNClNa (Fig. 2). We propose that ring opening of bromonium ion *trans*-**74** is faster (thus leading to overall *cis*-aziridination) due to hydrogen-bonded delivery of the nucleophile to the C-3 carbon (*trans*-diaxial opening of the bromonium ion). However, TsNClNa attack on the less sterically hindered C-2 of bromonium ion *cis*-**74** is competitive, accounting for the overall moderate levels of *cis*-stereoselectivity observed in these aziridinations. Presumably, using the more sterically hindered BusNClNa, the rate of ring-opening of bromonium ion *cis*-**74** is retarded significantly relative to that of *trans*-**74** which can still benefit from the hydrogen-bonded delivery.

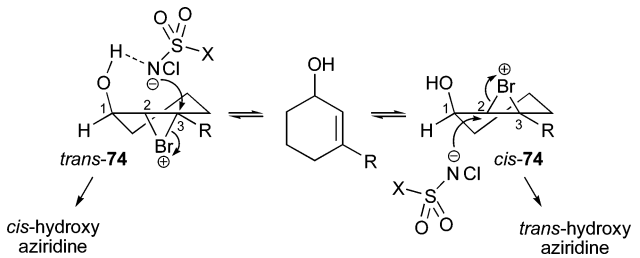


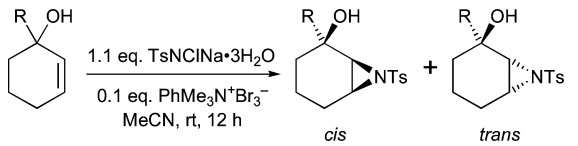
Fig. 2 Ring opening of bromonium ions *trans*-**74** and *cis*-**74**.

Aziridination of 1-substituted cyclic allylic alcohols

Next, the aziridination of 1-substituted allylic alcohols was studied using the TsNClNa·3H$_2$O conditions. The cyclohexene-derived allylic alcohols were generally well-behaved and the results are summarised in Table 3. In most cases, the reactions showed a moderate level of *cis*-stereoselectivity (*cis* : *trans* 60 : 40–75 : 25). As with the 3-substituted allylic alcohols (Table 2), the lowest stereoselectivity was obtained when R = *i*-Pr (**42**) (Table 3, entry 5). The relative stereochemistry of hydroxy aziridines **75** and **78** was established unequivocally as the *trans*-diastereomers underwent aza-Payne rearrangement during the purification by chromatography on silica gel (Scheme 6). In addition, hydroxy aziridine *cis*-**77** was independently prepared by *anti*-addition of allylMgCl to keto aziridine **81** (Scheme 6).

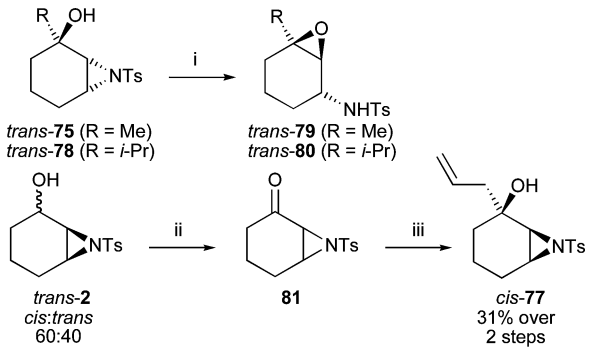
Our working model to rationalise the moderate levels of *cis*-stereoselectivity in the aziridination of 1-substituted cyclohexenols is depicted in Fig. 3. Reversible bromonium ion formation is followed by nucleophilic attack by the TsNClNa onto *trans*-**82** and *cis*-**82**. By analogy with the 3-substituted allylic alcohols (Fig. 2),

Table 3 Aziridination of 1-substituted cyclic allylic alcohols



Entry	R	SM	Product	*cis* : *trans*[a]	Yield of *cis* (%)[b]	Yield of *trans* (%)[b]
1	H	**1**	**2**	60 : 40	57	25
2	Me	**39**	**75**	75 : 25	67	17[c]
3	*n*-Bu	**40**	**76**	70 : 30	80[d]	—[d]
4	Allyl	**41**	**77**	65 : 35	46[d]	—[d]
5	*i*-Pr	**42**	**78**	55 : 45	49	20[c]

[a] Ratio determined by ^{1}H NMR spectroscopy of the crude product. [b] Yield after chromatography. [c] *trans*-**75** and *trans*-**78** underwent aza-Payne rearrangement during chromatography (see Scheme 6). [d] *cis*- and *trans*-hydroxy aziridines obtained as an inseparable mixture.



Scheme 6 *Reagents and conditions:* i, silica gel. ii, Dess–Martin periodinane, CH_2Cl_2, rt, 45 min. iii, AllylMgCl, THF, –78 °C.

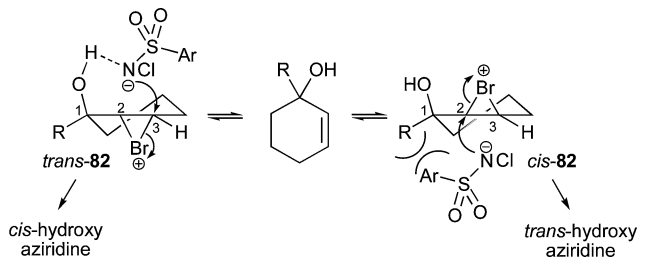


Fig. 3 Ring opening of bromonium ions *trans*-**82** and *cis*-**82**.

we propose the same hydrogen-bonded delivery of the TsNClNa to C-3 of *trans*-**82**. This is faster than ring opening of *cis*-**82** which suffers from a steric clash between the substituent (*R*) on C-1. Our model indicates *trans*-diaxial attack at C-2 of *cis*-**82**.

In contrast, aziridination of the 1-substituted cyclopentenols did not proceed in the expected manner. Under the standard aziridination conditions, no aziridine products were formed from **43**, **44** and **26** according to the ^{1}H NMR spectra of the crude products. Instead, in all three cases, the same type of product was generated as the major one. Eventually, after obtaining the X-ray crystal structure of one of them (*cis*-**83**, Fig. 4), the major products were identified as epoxy sulfonamides *cis*-**83**, **85**, and **87** (46–54% yield) (Scheme 7). Notably, this *epoxidation* did not occur with the unsubstituted cyclopentenol **35** and with the cyclohexenols (Table 3). On close inspection of the crude products by ^{1}H NMR

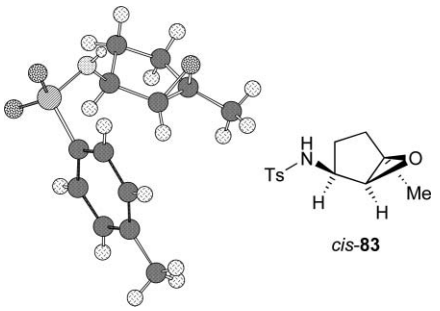
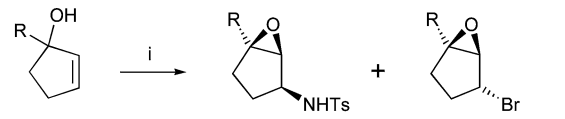


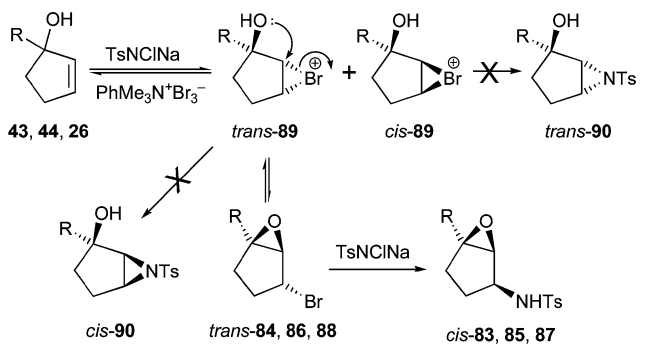
Fig. 4 X-Ray crystal structure of *cis*-**83**.



Scheme 7 *Reagents and conditions:* i, 1.1 eq. $TsNClNa{\cdot}3H_2O$, 0.1 eq. $PhMe_3N^+Br_3^-$, MeCN, rt, 12 h.

spectroscopy, it was clear that another type of product was also formed. However, they were unstable to chromatography and could not be isolated in pure form. From a mechanistic analysis (*vide infra*), we suspected that they might be epoxy bromides *trans*-**84**, **86** and **88**. This was confirmed by an independent synthesis of epoxy bromide *trans*-**84**: Henbest-like *cis*-epoxidation of allylic alcohol **43** was followed by bromide formation using PPh_3–CBr_4 to give crude *trans*-**84** which had the same ^{1}H NMR spectrum as the by-product from the attempted aziridination of allylic alcohol **43**.

A mechanism that accounts for the formation of epoxy sulfonamides *cis*-**83**, **85** and **87** together with the corresponding epoxy bromides *trans*-**84**, **86** and **88** is shown in Scheme 8. The first step is reversible formation of bromonium ions *trans*-**89** and *cis*-**89** which would normally be ring-opened by TsNClNa to ultimately give the corresponding hydroxy aziridines *cis*-**90** and *trans*-**90**. This process does not happen with cyclopentenols **43**, **44** and **26**. Instead, we propose that reversible epoxide formation occurs from bromonium ion *trans*-**89** to give the epoxy bromides *trans*-**84**, **86** and **88** which subsequently undergo a slow and irreversible nucleophilic substitution reaction with TsNClNa to give epoxy sulfonamides *cis*-**83**, **85** and **87**. Since our mechanistic conjecture



Scheme 8 Mechanistic suggestion for the formation of *cis*-**83**, **85** and **87**.

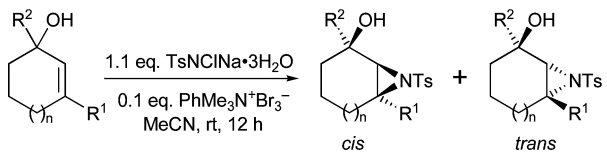
indicates that the *trans*-epoxy bromides are intermediates in the formation of the *cis*-epoxy sulfonamides, it should be possible to increase the yields of the *cis*-epoxy sulfonamides by increasing the reaction time. This did indeed prove to be the case in one example. Whereas reaction of allylic alcohol **26** with $TsNClNa{\cdot}3H_2O$ and $PhMe_3N^+Br_3^-$ in MeCN for 12 hours gave epoxy sulfonamide *cis*-**87** in 54% yield, a 36 hour reaction time furnished the same product in 97% yield.

Aziridination of 1,3-disubstituted cyclic allylic alcohols

Finally, the aziridination of 1,3-disubstituted cyclic allylic alcohols was studied. The results are presented in Table 4. Remarkably, in seven out of the eight allylic alcohols that were subjected to aziridination, single *cis*-diastereomers of hydroxy aziridines were generated (*cis*-**91–94** and *cis*-**96–98**, Table 4, entries 1–4 and 6–8). In these seven cases, there was no evidence of any *trans*-hydroxy aziridines in the ^{1}H NMR spectra of the crude products and similar results were obtained for the five- and six-membered ring allylic alcohols. The only disappointing result was with allylic alcohol **49** in which a 65 : 35 mixture of hydroxy aziridines *cis*- and *trans*-**95** was formed (Table 4, entry 5).

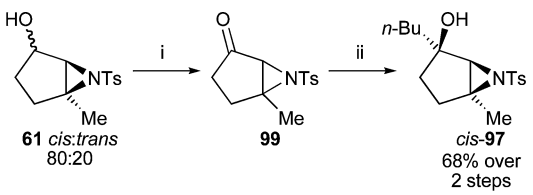
The relative stereochemistry of these hydroxy aziridines was established in the following way. The structure of one of the cyclohexenol-derived hydroxy aziridines (*cis*-**93**) was determined by X-ray crystallography (Fig. 5). In addition, the cyclopentenol-derived hydroxy aziridine *cis*-**97** was synthesised by *anti*-addition of *n*-BuMgBr to keto aziridine **99** (Scheme 9). The stereochemistry of the other hydroxy aziridines in Table 4 were assigned by analogy.

Table 4 Aziridination of 1,3-disubstituted cyclic allylic alcohols



Entry	*n*	R^1	R^2	SM	Product	*cis* : *trans*[a]	Yield of *cis* (%)[b]
1	1	Me	Me	**45**	**91**	>98 : 2	70
2	1	Me	*n*-Bu	**46**	**92**	>98 : 2	90
3	1	*n*-Bu	Me	**47**	**93**	>98 : 2	73
4	1	Allyl	*n*-Bu	**48**	**94**	>98 : 2	53
5	1	*i*-Pr	*n*-Bu	**49**	**95**	65 : 35	23[c]
6	0	Me	Me	**50**	**96**	>98 : 2	77
7	0	Me	*n*-Bu	**51**	**97**	>98 : 2	75
8	0	Allyl	*n*-Bu	**52**	**98**	>98 : 2	32

[a] Ratio determined by ^{1}H NMR spectroscopy of the crude product. [b] Yield after chromatography. [c] *trans*-**95** not isolated after chromatography.



Scheme 9 *Reagents and conditions:* i, Dess–Martin periodinane, CH_2Cl_2, rt, 45 min. ii, *n*-BuMgCl, THF, –78 °C.

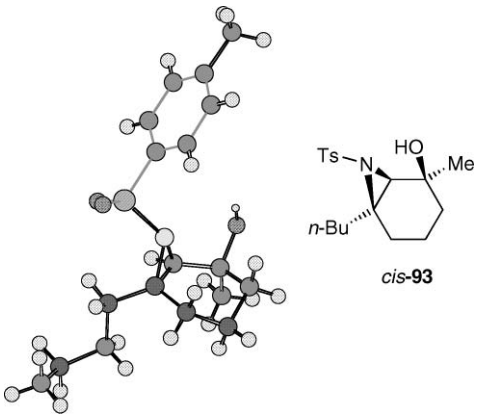


Fig. 5 X-Ray crystal structure of *cis*-**93**.

The complete *cis*-stereoselective aziridination of the 1,3-disubstituted allylic alcohols can be rationalised as shown in Fig. 6. Presumably, ring-opening of bromonium ion *cis*-**100** is very slow due to the steric hindrance from the R^1 *and* R^2 substituents. Attack at C-2 will be disfavoured due to a steric clash with the R^2 substituent whilst attack at the tertiary C-3 position seems unlikely due to steric hindrance. This is in contrast to 3-substituted allylic alcohols (Fig. 2) and 1-substituted allylic alcohols (Fig. 3) in which steric hindrance is relieved such that nucleophilic attack by TsNClNa on the *cis*-bromonium ions is at least possible (albeit slower than attack on the *trans*-bromonium ions).

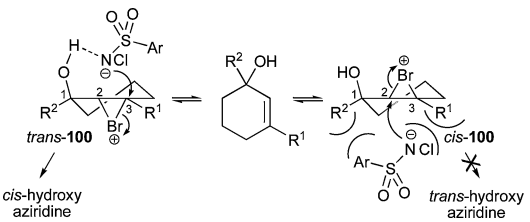


Fig. 6 Ring opening of bromonium ions *trans*-**100** and *cis*-**100**.

Conclusion

In summary, a wide range of cyclic allylic alcohols with different substitution patterns has been aziridinated under Sharpless conditions and the sense and degree of stereoselectivity established. In general, *cis*-stereoselectivity predominated and this has allowed easy access to a significant number of diastereomerically pure *cis*-hydroxy aziridines after purification by chromatography. These types of *cis*-hydroxy aziridines are interesting synthetic building blocks and organolithium-mediated reactions of their methyl ethers have proved useful for further synthetic efforts.[2,4,5] Through our studies, the full scope and limitations of the Sharpless aziridination of cyclic allylic alcohols has been determined. An unexpected aspect of our investigation was the complete *cis*-stereoselectivity observed in the aziridination of seven 1,3-disubstituted allylic alcohols. A mechanistic rationale for this (and the other aziridinations) involving reversible *cis*- and *trans*-bromonium ion formation and subsequent different rates of ring-opening of these bromonium ions has been forwarded.

Experimental

General

All non-aqueous reactions were carried out under O_2-free N_2 or Ar using oven-dried glassware. CH_2Cl_2 was dried on an Mbraun SPS solvent purification system. Et_2O and THF were distilled from sodium and benzophenone. Petrol refers to the fraction of petroleum ether boiling in the range 40–60 °C and was purchased in Winchester quantities. Brine refers to a saturated aqueous solution of NaCl. Water is distilled water. Flash chromatography was carried out using Fluka Chemie GmbH silica (220–440 mesh). Thin layer chromatography was carried out using commercially available Merck F_{254} aluminium-backed silica plates. Proton (400 or 270 MHz) and carbon (100.6 or 67.9 MHz) NMR spectra were recorded on a Jeol ECX-400 instrument or a Jeol EX-270 instrument using an internal deuterium lock. For samples recorded as solutions in $CDCl_3$, chemical shifts are quoted in parts per million relative to $CHCl_3$ (δ_H 7.27) and $CDCl_3$ (δ_C 77.0, central line of triplet). Carbon NMR spectra were recorded with broad band proton decoupling and were assigned using DEPT experiments. Coupling constants (J) are quoted in Hertz. Melting points were carried out on a Gallenkamp melting point apparatus. Infra-red spectra were recorded on a Nicolet IR100 FT-IR spectrometer or an ATI Mattson Genesis FT-IR spectrometer. Chemical ionization high and low resolution mass spectra were recorded on a Fisons Analytical (VG) Autospec spectrometer. Electrospray high and low resolution mass spectra were recorded on a Bruker Daltonics micrOTOF spectrometer.

The synthesis of all of the allylic alcohols is described in the ESI.†

General procedure for aziridination. $PhMe_3NBr_3$ (0.1 eq.) was added in one portion to a stirred suspension of chloramine-T trihydrate ($TsNClNa{\cdot}3H_2O$) (1.1 eq.) or BucNClNa (1.2 eq.) and cyclic allylic alcohol (1.0 mmol) in MeCN (5 mL) at rt under N_2. After stirring at rt for 12 h, the resulting suspension was filtered through a silica plug and washed well with Et_2O. The filtrate was evaporated under reduced pressure to give the crude product.

7-[(4-Methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptan-2-ol *cis*-2 and *trans*-2. Using the general procedure, allylic alcohol **1** (543 mg, 5.5 mmol), chloramine-T trihydrate (1.70 g, 6.0 mmol) and $PhMe_3NBr_3$ (210 mg, 0.6 mmol) in MeCN (25 mL) gave the crude product, which contained a 60 : 40 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**2** and *trans*-**2**. Purification by flash chromatography on silica with petrol–Et_2O (3 : 7) as eluent gave hydroxy aziridine *trans*-**2** (363 mg, 25%) as an off-white solid, mp 76–77 °C (lit.,[6] 69–70 °C), R_F(3 : 7 petrol–Et_2O) 0.13; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.36 (br d, J = 8.0, 2H, *o*-C_6H_4Me), 4.00–3.89 (m, 1H, CHO), 3.08–3.00 (m, 1H, CHN), 2.95 (d, J = 7.0, 1H, CHN), 2.44 (s, 3H, Me), 1.89–1.63 (m, 3H, 3 × CH) and 1.60–1.26 (m, 3H, 3 × CH) and hydroxy aziridine *cis*-**2** (831 mg, 57%) as a colourless oil, R_F(3 : 7 petrol–Et_2O) 0.09; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.32 (br d, J = 8.0, 2H, *o*-C_6H_4Me), 4.00–3.89 (m, 1H, CHO), 3.20 (br s, 2H, 2 × CHN), 2.45 (s, 3H, Me), 1.85–1.72 (m, 2H, 2 × CH), 1.61–1.46 (m, 2H, 2 × CH), 1.42–1.30 (m, 1H, CH), 1.29–1.14 (m, 1H, CH). Spectroscopic data consistent with those reported in the literature.[6]

6-Methyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptan-2-ol *cis*-53 and *trans*-53. Using the general procedure, allylic alcohol **28** (790 mg, 7.0 mmol), chloramine-T trihydrate (2.18 g, 7.7 mmol) and $PhMe_3NBr_3$ (262 mg, 0.7 mmol) in MeCN (35 mL) gave the crude product, which contained a 75 : 25 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**53** and *trans*-**53**. Purification by flash chromatography on silica with $CHCl_3$–acetone (97 : 3) as eluent gave hydroxy aziridine *cis*-**53** (1.34 g, 68%) as a white solid, mp 74–76 °C; R_F(9 : 1 $CHCl_3$–acetone) 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5, 2H, *m*-C_6H_4Me), 7.32 (d, J = 8.5, 2H, *o*-C_6H_4Me), 3.99 (app. sextet, J = 5.0, 1H, CHO), 3.36 (d, J = 5.0, 1H, CHN), 2.44 (s, 3H, Me), 2.06–2.00 (m, 1H, CH), 1.76 (s, 3H, Me), 1.55–1.41 (m, 2H, 2 × CH), 1.40–1.38 (m, 2H, 2 × CH), 1.28–1.22 (m, 2H, CH and OH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.2 (*ipso*-$C_6H_4SO_2$), 137.6 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 127.4 (*o*-C_6H_4Me), 63.9 (CHO), 54.1 (CN), 51.7 (CHN), 31.3 (CH_2), 29.6 (CH_2), 21.6 (Me), 20.2 (Me), 16.7 (CH_2); MS (CI, NH_3) m/z 299 [$(M + NH_4)^+$, 30], 282 (100), 189 (15), 126 (15); HRMS (CI, NH_3) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}NO_3S$, 282.1164; found, 282.1159. Diagnostic signals for hydroxy aziridine *trans*-**53**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (br t, J = 6.5, 1H, CHO), 3.05 (s, 1H, CHN).

6-Butyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptan-2-ol *cis*-54 and *trans*-54. Using the general procedure, allylic alcohol **29** (175 mg, 1.1 mmol), chloramine-T trihydrate (352 mg, 1.2 mmol) and $PhMe_3NBr_3$ (42 mg, 0.1 mmol) in MeCN (6 mL) gave the crude product, which contained a 70 : 30 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**54** and *trans*-**54**. Purification by flash chromatography on silica with CH_2Cl_2–acetone (95 : 5) as eluent gave hydroxy aziridine *cis*-**54** (165 mg, 45%) as a colourless oil, R_F(95 : 5 CH_2Cl_2–acetone) 0.4; IR (film) 3520 (OH), 2954, 2869, 1455, 1404, 1319 (SO_2), 1155 (SO_2), 1090, 976, 931 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5, 2H, *m*-C_6H_4Me), 7.32 (br d, J = 8.5, 2H, *o*-C_6H_4Me), 3.92 (app. sextet, J = 5.0, 1H, CHO), 3.29 (d, J = 5.0, 1H, CHN), 2.42 (s, 3H, Me), 2.11–1.98 (m, 2H, 2 × CH), 1.88 (ddd, J = 14.5, 8.0, 5.0, 1H, CH), 1.69 (dt, J = 14.5, 6.0, 1H, CH), 1.59–1.17 (m, 8H, 4 × CH_2), 0.92 (t, J = 7.0, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.1 (*ipso*-$C_6H_4SO_2$), 137.6 (*ipso*-C_6H_4Me), 129.6 (*m*-C_6H_4Me), 127.4 (*o*-C_6H_4Me), 64.7 (CHO), 58.6 (CN), 51.3 (CHN), 33.1 (CH_2), 29.4 (CH_2), 28.9 (CH_2), 28.0 (CH_2), 22.6 (CH_2), 21.6 (Me), 17.8 (CH_2), 14.0 (Me); MS (CI, NH_3) m/z 324 [$(M + H)^+$, 55], 168 (100), 153 (45), 140 (15); HRMS (CI, NH_3) m/z: $[M + H]^+$ calcd for $C_{17}H_{25}NO_3S$, 324.1633; found, 324.1633 and a mixture of hydroxy aziridine *trans*-**54** and $TsNH_2$ (102 mg). This mixture was dissolved in Et_2O (2.5 mL) and hexane (2.5 mL) was added. The resulting mixture was placed in the freezer for 12 h. The resulting suspension was filtered, and the filtrate was evaporated under reduced pressure to give hydroxy aziridine *trans*-**54** (46 mg, 13%) as a colourless oil, R_F(95 : 5 CH_2Cl_2–acetone) 0.3; IR (film) 3503 (OH), 2954, 2871, 1455, 1319 (SO_2), 1156 (SO_2), 1089, 987 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.28 (br d, J = 8.0, 2H, *o*-C_6H_4Me), 3.92 (br dt, J = 8.0, 5.0, 1H, CHO), 3.01 (s, 1H, CHN), 2.41 (s, 3H, Me), 2.05–1.91 (m, 3H, 3 × CH), 1.77–1.71 (m, 1H, CH), 1.66 (ddd, J = 15.0, 9.5, 5.5, 1H, CH), 1.58–1.20 (m, 6H, 6 × CH_2), 1.10–1.01 (m, 1H, 1 × CH), 0.91 (t, J = 7.0, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.6 (*ipso*-$C_6H_4SO_2$), 138.4 (*ipso*-C_6H_4Me), 129.4 (*m*-C_6H_4Me), 127.0 (*o*-C_6H_4Me), 65.6 (CHO), 56.5 (CN), 51.1 (CHN), 32.9 (CH_2), 29.9 (CH_2), 28.9 (CH_2), 28.3 (CH_2), 22.5 (CH_2), 21.5 (Me), 15.7 (CH_2), 13.9 (Me); MS (CI, NH_3) m/z 324 [$(M + H)^+$, 100], 306 (20), 153 (50); HRMS (CI, NH_3) m/z: $[M + H]^+$ calcd for $C_{17}H_{25}NO_3S$, 324.1633; found, 324.1628.

6-Allyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptan-2-ol *cis*-55 and *trans*-55. Using the general procedure, allylic alcohol **30** (138 mg, 1.0 mmol), chloramine-T trihydrate (310 mg, 1.1 mmol) and $PhMe_3NBr_3$ (38 mg, 0.1 mmol) in MeCN (5 mL) gave the crude product, which contained a 65 : 35 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**55** and *trans*-**55**. Purification by flash chromatography on silica with petrol–Et_2O (1 : 1) as eluent gave a 65 : 35 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**55** and *trans*-**55** (217 mg, 71%) as a colourless oil, R_F(1 : 1 petrol–Et_2O) 0.1. Further purification by flash chromatography on silica with CH_2Cl_2–acetone (95 : 5) as eluent gave a sample of hydroxy aziridine *cis*-**55** as a colourless oil, R_F(9 : 1 CH_2Cl_2–acetone) 0.5; IR (film) 3521 (OH), 2944, 2865, 1319 (SO_2), 1154 (SO_2), 1090, 977, 930 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5, 2H, *m*-C_6H_4Me), 7.31 (br d, J = 8.5, 2H, *o*-C_6H_4Me), 5.83 (ddt, J = 17.0, 10.0, 7.0, 1H, =CH), 5.18–5.12 (m, 2H, =CH_2), 3.97–3.91 (m, 1H, CHO), 3.37 (d, J = 4.5, 1H, CHN), 2.81 (app. dt, J = 7.0, 1.0, 2H, CH_2CH=CH_2), 2.42 (s, 3H, Me), 1.87–1.78 (m, 1H, CH), 1.73–1.66 (m, 1H, CH), 1.50–1.37 (m, 2H, 2 × CH), 1.32–1.23 (m, 2H, CH and OH), 1.21–1.12 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.8 (*ipso*-$C_6H_4SO_2$), 138.1 (*ipso*-C_6H_4Me), 133.9 (=CH), 129.5 (*m*-C_6H_4Me), 127.0 (*o*-C_6H_4Me), 118.4 (=CH_2), 65.6 (CHO), 54.8 (C(N)), 50.7 (CHN), 37.8 (CH_2), 29.9 (CH_2), 28.2 (CH_2), 21.6 (Me), 15.6 (CH_2); MS (CI, NH_3) m/z 308 [$(M + H)^+$, 90], 152 (100), 137 (25), 124 (20); HRMS (CI, NH_3) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}NO_3S$, 308.1320; found, 308.1317 and a sample of hydroxy aziridine *trans*-**55** as a colourless oil, R_F(9 : 1 CH_2Cl_2–acetone) 0.4; IR (film) 3501 (OH), 2943, 1319 (SO_2), 1304, 1290, 1156 (SO_2), 1089, 988 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.30 (br d, J = 8.0, 2H, *o*-C_6H_4Me), 5.92–5.82 (m, 1H, =CH), 5.21–5.12 (m, 2H, =CH_2), 3.70 (br t, J = 7.0, 1H, CHO), 3.07 (s, 1H, CHN), 2.80 (app. d, J = 7.0, 2H, CH_2CH=CH_2), 2.43 (s, 3H, Me), 1.90 (dt, J = 14.5, 5.0, 1H, CH), 1.75 (dt, J = 13.0, 7.0, 1H, CH), 1.67 (ddd, J = 14.5, 9.5, 5.5, 1H, CH), 1.44–1.36 (m, 1H, CH), 1.29–1.18 (m, 2H, CH and OH), 1.09–1.00 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.2 (*ipso*-$C_6H_4SO_2$), 137.4 (*ipso*-C_6H_4Me), 133.6 (=CH), 129.6 (*m*-C_6H_4Me), 127.4 (*o*-C_6H_4Me), 118.6 (=CH_2), 64.7 (CHO), 56.9 (C(N)), 50.9 (CHN), 37.9 (CH_2), 29.2 (CH_2), 27.7 (CH_2), 21.6 (Me); MS (CI, NH_3) m/z 308 [$(M + H)^+$, 70], 152 (100), 137 (45), 124 (20); HRMS (CI, NH_3) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}NO_3S$, 308.1320; found, 308.1318.

6-Homoallyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]-heptan-2-ol *cis*-56 and *trans*-56. Using the general procedure, allylic alcohol **31** (250 mg, 1.64 mmol), chloramine-T trihydrate (509 mg, 1.81 mmol) and $PhMe_3NBr_3$ (62 mg, 0.16 mmol) in MeCN (10 mL) gave the crude product as a solution in Et_2O–MeCN. This was washed with 2 M $NaOH_{(aq)}$ (5 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product, which contained a 70 : 30 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**56** and *trans*-**56**. Purification by flash chromatography on silica with CH_2Cl_2–acetone (96 : 4) as eluent gave hydroxy aziridine *cis*-**56** (106 mg,

34%) as a pale yellow oil, R_F(96 : 4 CH_2Cl_2–acetone) 0.3; IR ($CHCl_3$) 3610 (OH), 2949, 1641 (C=C), 1456, 1319 (SO_2), 1159 (SO_2), 1092 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.33 (d, J = 8.0, 2H, *o*-C_6H_4Me), 5.87–5.76 (m, 1H, C*H*=CH_2), 5.06 (dd, J = 17.5, 1.0, 1H, CH=CH_AH_B), 5.02 (br d, J = 10.5, 1H, CH=CH_AH_B), 3.92 (sextet, J = 5.0, 1H, CHO), 3.31 (d, J = 5.0, 1H, CHN), 2.43 (s, 3H, Me), 2.40–2.37 (m, 1H, CH), 2.24–2.15 (m, 3H, 3 × CH), 1.89 (ddd, J = 12.0, 7.5, 5.0, 1H, CH), 1.72 (dt, J = 15.0, 6.0, 1H, CH), 1.54–1.39 (m, 2H, 2 × CH), 1.33–1.16 (m, 2H, 2 × CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.1 (*ipso*-$C_6H_4SO_2$), 137.6 (*ipso*-C_6H_4Me), 137.2 (=CH), 129.7 (*m*-C_6H_4Me), 127.4 (*o*-C_6H_4Me), 115.7 (=CH_2), 64.7 (CHO), 57.7 (CN), 51.5 (CHN), 32.4 (CH_2), 30.9 (CH_2), 29.4 (CH_2), 27.8 (CH_2), 21.6 (Me), 17.8 (CH_2); MS (CI, NH_3) *m*/*z* 322 [(M + H)$^+$, 100], 304 (20), 249 (6), 189 (9), 166 (73), 151 (49), 133 (5); HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{23}NO_3S$, 322.1477; found, 322.1479 and hydroxy aziridine *trans*-**56** (37 mg, 12%) as a pale yellow oil, R_F(96 : 4 CH_2Cl_2–acetone) 0.2; IR ($CHCl_3$) 3601 (OH), 3018, 2951, 1450, 1317 (SO_2), 1159 (SO_2), 1090, 987 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.30 (d, J = 8.0, 2H, *o*-C_6H_4Me), 5.84 (ddt, J = 17.0, 10.5, 6.5, 1H, C*H*=CH_2), 5.08 (dd, J = 17.5, 1.5, 1H, CH=CH_AH_B), 5.01 (br d, J = 10.5, 1H, CH=CH_AH_B), 3.69 (dt, J = 7.5, 5.0, 1H, CHO), 3.04 (s, 1H, CHN), 2.43 (s, 3H, Me), 2.39–2.35 (m, 1H, CH), 2.30–2.09 (m, 3H, 3 × CH), 1.95 (dt, J = 15.0, 5.0, 1H, CH), 1.81–1.66 (m, 2H, 2 × CH), 1.46–1.38 (m, 1H, CH), 1.32–1.23 (m, 1H, CH), 1.10–1.01 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.7 (*ipso*-$C_6H_4SO_2$), 138.3 (*ipso*-C_6H_4Me), 137.5 (=CH), 129.5 (*m*-C_6H_4Me), 127.0 (*o*-C_6H_4Me), 115.5 (=CH_2), 65.6 (CHO), 55.7 (CN), 51.1 (CHN), 32.2 (CH_2), 31.0 (CH_2), 30.0 (CH_2), 28.2 (CH_2), 21.5 (Me), 15.6 (CH_2); MS (CI, NH_3) *m*/*z* 322 [(M + H)$^+$, 100], 304 (26), 189 (75), 168 (42), 166 (43), 151 (82), 139 (36), 133 (70), 108 (16); HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{23}NO_3S$, 322.1477; found, 322.1475.

***N*-(6-Hydroxy-2-isopropylcyclohex-2-en-1-yl)-4-methylbenzenesulfonamide *cis*-70 and *trans*-70.** Using the general procedure, allylic alcohol **32** (108 mg, 0.8 mmol), chloramine-T trihydrate (239 mg, 0.8 mmol) and $PhMe_3NBr_3$ (29 mg, 0.1 mmol) in MeCN (4 mL) gave the crude product, which contained a 55 : 45 mixture (by ^1H NMR spectroscopy) of hydroxy aziridines *cis*-**57** and *trans*-**57**. Purification by flash chromatography on silica with hexane–EtOAc (7 : 3) as eluent gave a 60 : 40 mixture (by ^1H NMR spectroscopy) of alcohols *cis*-**70** and *trans*-**70** (152 mg, 64%) as a pale yellow solid. Further purification by flash chromatography on silica with hexane–$CHCl_3$–MeOH (60 : 32 : 8) gave a pure sample of alcohol *cis*-**70** as a white solid, mp 115–117 °C; R_F(60 : 32 : 8 hexane–$CHCl_3$–MeOH) 0.23; IR (Nujol mull) 3435 (OH), 3272 (NH), 1306 (SO_2), 1160 (SO_2), 1096, 1067, 931, 815 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.32 (d, J = 8.0, 2H, *o*-C_6H_4Me), 5.49 (t, J = 3.5, 1H, =CH), 4.64 (d, J = 8.0, 1H, NH), 3.85 (dd, J = 8.0, 4.0, 1H, CHN), 3.67–3.60 (m, 1H, CHO), 2.64 (d, J = 7.0, 1H, OH), 2.42 (s, 3H, Me), 2.19–2.10 (m, 1H, CH), 2.05–1.96 (m, 1H, CH), 1.75 (ddt, J = 3.0, 6.0, 3.5, 1H, CH), 1.68 (septet, J = 7.0, 1H, C*H*Me_2), 1.59–1.49 (m, 1H, CH), 0.86 (d, J = 7.0, 3H, CH*Me*$_A$$Me_B$), 0.68 (d, J = 7.0, 3H, CHMe_A*Me*$_B$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.7 (*ipso*-$C_6H_4SO_2$), 141.1 (=C), 137.4 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 127.2 (*o*-C_6H_4Me), 123.1 (=CH), 68.7 (CHO), 54.6 (CHN), 29.8 (*C*HMe_2), 25.9 (CH_2), 23.5 (CH_2), 22.4 (Me), 21.5 (Me), 20.9 (Me); MS (CI, NH_3) *m*/*z* 327 [(M + NH_4)$^+$, 70], 310 (20), 189 (100), 156 (20); HRMS (CI, NH_3) *m*/*z*: [M + NH_4]$^+$ calcd for $C_{16}H_{23}NO_3S$, 327.1742; found, 327.1745 and alcohol *trans*-**70** as a white solid, mp 114–116 °C; R_F(60 : 32 : 8 hexane–$CHCl_3$–MeOH) 0.20; IR (Nujol mull) 3493 (OH), 3271 (NH), 1306 (SO_2), 1158 (SO_2), 1096, 1050 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.31 (d, J = 8.0, 2H, *o*-C_6H_4Me), 5.59 (t, J = 4.0, 1H, =CH), 4.71 (d, J = 8.0, 1H, NH), 3.88 (br s, 1H, CHO), 3.59 (dd, J = 8.0, 4.5, 1H, CHN), 2.42 (s, 3H, Me), 2.34 (br s, 1H, OH), 2.14–1.96 (m, 2H, 2 × CH), 1.84–1.76 (m, 2H, 2 × CH), 1.66–1.58 (m, 1H, CH), 0.89 (d, J = 7.0, 3H, CH*Me*$_A$$Me_B$), 0.62 (d, J = 7.0, 3H, CHMe_A*Me*$_B$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.6 (*ipso*-$C_6H_4SO_2$), 139.5 (=C), 137.3 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 127.1 (*o*-C_6H_4Me), 123.5 (=CH), 70.3 (CHO), 55.7 (CHN), 29.8 (*C*HMe_2), 24.5 (CH_2), 22.3 (Me), 21.5 (Me), 20.9 (Me), 20.7 (CH_2); MS (CI, NH_3) *m*/*z* 327 [(M + NH_4)$^+$, 60], 189 (100); HRMS (CI, NH_3) *m*/*z*: [M + NH_4]$^+$ calcd for $C_{16}H_{23}NO_3S$, 327.1742; found, 327.1747.

6-[(4-Methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]hexan-2-ol *cis*-60 and *trans*-60. Using the general procedure, allylic alcohol **35** (400 mg, 4.76 mmol), chloramine-T trihydrate (1.47 g, 5.23 mmol) and $PhMe_3NBr_3$ (179 mg, 0.48 mmol) in MeCN (20 mL) gave the crude product, which contained a 60 : 40 mixture (by ^1H NMR spectroscopy) of hydroxy aziridines *cis*-**60** and *trans*-**60**. Purification by flash chromatography with petrol–Et_2O (2 : 8) as eluent gave hydroxy aziridine *trans*-**60** (275 mg, 23%) as a white solid, mp 84–85 °C; R_F(Et_2O) 0.4; IR (CH_2Cl_2) 3600 (OH), 3064, 2929, 2862, 1323 (SO_2), 1161 (SO_2) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.34 (br d, J = 8.0, 2H, *o*-C_6H_4Me), 4.32 (br s, 1H, CHO), 3.41 (br dd, J = 5.0, 1.0, 1H, CHN), 3.31 (br d, J = 5.0, 1H, CHN), 2.45 (s, 3H, Me), 1.93–1.91 (m, 2H, 2 × CH), 1.83 (br s, 1H, OH), 1.75–1.53 (m, 2H, 2 × CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.5 (*ipso*-$C_6H_4SO_2$), 135.1 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 127.7 (*o*-C_6H_4Me), 71.8 (CHO), 48.4 (CHN), 45.9 (CHN), 30.3 (CH_2), 24.9 (CH_2), 21.6 (Me); MS (CI, NH_3) *m*/*z* 271 [(M + NH_4)$^+$, 72], 254 [(M + H)$^+$, 100]; HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{12}H_{15}NO_3S$, 254.0851; found, 254.0844 and hydroxy aziridine *cis*-**60** (530 mg, 44%) as a colourless oil, R_F(Et_2O) 0.3; IR (CH_2Cl_2) 3600 (OH), 3064, 2929, 2862, 1323 (SO_2), 1161 (SO_2) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.35 (br d, J = 8.0, 2H, *o*-C_6H_4Me), 4.38–4.23 (m, 1H, CHO), 3.39 (br dd, J = 5.0, 3.0, 1H, CHN), 3.34 (br dd, J = 5.0 and 2.5, 1H, CHN), 2.45 (s, 3H, Me), 2.03 (dd, J = 13.5, 6.0, 1H, CH), 1.96 (app. dt, J = 13.5, 8.0, 1H, CH), 1.80–1.63 (m, 2H, CH and OH), 1.32–1.19 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.5 (*ipso*-$C_6H_4SO_2$), 135.2 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 127.7 (*o*-C_6H_4Me), 72.5 (CHO), 49.1 (CHN), 45.2 (CHN), 28.5 (CH_2), 25.7 (CH_2), 21.6 (Me); MS (CI, NH_3) *m*/*z* 271 [(M + NH_4)$^+$, 100], 254 [(M + H)$^+$, 80]; HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{12}H_{15}NO_3S$, 254.0851; found, 254.0845.

5-Methyl-6-[(4-methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]hexan-2-ol *cis*-61 and *trans*-61. Using the general procedure, allylic alcohol **36** (260 mg, 2.7 mmol), chloramine-T trihydrate (822 mg, 2.9 mmol) and $PhMe_3NBr_3$ (102 mg, 0.3 mmol) in MeCN (10 mL) gave the crude product, which contained an 85 : 15 mixture (by

^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**61** and *trans*-**61**. Purification by flash chromatography on silica with petrol–Et_2O (1 : 4) as eluent gave hydroxy aziridine *trans*-**61** (82 mg, 12%) as a colourless oil, R_F(1 : 4 petrol–Et_2O) 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.30 (d, J = 8.0, 2H, *o*-C_6H_4Me), 4.30 (d, J = 4.5, 1H, CHO), 3.32 (s, 1H, CHN), 2.44 (s, 3H, Me), 2.35–2.23 (m, 1H, CH), 1.96–1.93 (m, 1H, CH), 1.83 (s, 3H, Me), 1.63–1.56 (m, 2H, CH and OH), 1.25–1.14 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.8 (*ipso*-$C_6H_4SO_2$), 137.8 (*ipso*-C_6H_4Me), 129.5 (*m*-C_6H_4Me), 127.2 (*o*-C_6H_4Me), 72.9 (CHO), 58.2 (CN), 54.6 (CHN), 32.6 (CH_2), 31.4 (CH_2), 21.6 (Me), 14.9 (Me); MS (CI, NH_3) m/z 285 [$(M + NH_4)^+$, 100], 268 (12), 250 (21), 189 (55), 112 (100); HRMS (CI, NH_3) m/z: $[M + NH_4]^+$ calcd for $C_{13}H_{17}NO_3S$, 285.1272; found, 285.1273 and hydroxy aziridine *cis*-**61** (446 mg, 63%) as a white solid, mp 104–107 °C; R_F(1 : 4 petrol–Et_2O) 0.2; IR ($CDCl_3$) 3600 (OH), 1321 (SO_2), 1159 (SO_2), 1092 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.33 (d, J = 8.0, 2H, *o*-C_6H_4Me), 4.29 (dtd, J = 10.0, 8.0, 3.0, 1H, CHO), 3.44 (d, J = 3.0, 1H, CHN), 2.44 (s, 3H, Me), 2.15 (dd, J = 14.0, 8.0, 1H, CH), 1.95 (dt, J = 13.5, 8.0, 1H, CH), 1.83 (s, 3H, Me), 1.60 (ddd, J = 14.0, 10.5, 8.0, 1H, CH), 1.20 (ddt, J = 13.5, 10.5, 8.0, 1H, CH), 1.06 (d, J = 10.0, 1H, OH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.0 (*ipso*-$C_6H_4SO_2$), 137.8 (*ipso*-C_6H_4Me), 129.6 (*m*-C_6H_4Me), 127.1 (*o*-C_6H_4Me), 73.1 (CHO), 57.3 (CN), 55.8 (CHN), 33.4 (CH_2), 29.8 (CH_2), 21.6 (Me), 15.3 (Me); MS (CI, NH_3) m/z 268 [$(M + H)^+$, 26], 250 (16), 112 (100); HRMS (CI, NH_3) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}NO_3S$, 268.1004; found, 268.1007.

5-Allyl-6-[(4-methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]hexan-2-ol *cis*-62 and *trans*-62. Using the general procedure, allylic alcohol **37** (80 mg, 0.6 mmol), chloramine-T trihydrate (200 mg, 0.7 mmol) and $PhMe_3NBr_3$ (24 mg, 0.1 mmol) in MeCN (3.5 mL) gave the crude product, which contained a 65 : 35 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**62** and *trans*-**62**. Purification by flash chromatography on silica with hexane–Et_2O (3 : 7) as eluent gave hydroxy aziridine *trans*-**62** (42 mg, 22%) as a colourless oil, R_F(3 : 7 hexane–Et_2O) 0.22; IR (film) 3501 (OH), 2924, 1599, 1436, 1318 (SO_2), 1154 (SO_2), 1092, 990 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5, 2H, *m*-C_6H_4Me), 7.30 (d, J = 8.5, 2H, *o*-C_6H_4Me), 5.93 (ddt, J = 17.0, 10.0, 7.0, 1H, =CH), 5.23 (app. dq, J = 17.0, 1.5, 2H, =CH_AH_B), 5.15 (ddt, J = 10.0, 1.5, 1.0, 1H, =CH_AH_B), 4.15 (d, J = 5.0, 1H, CHO), 3.35 (s, 1H, CHN), 3.07 (br dd, J = 15.0, 7.0, 1H, CH_AH_BCH=CH_2), 2.99 (br dd, J = 15.0, 7.0, 1H, CH_AH_BCH=CH_2), 2.43 (s, 3H, Me), 1.99–1.88 (m, 2H, 2 × CH), 1.68–1.58 (m, 1H, CH), 1.51 (ddd, J = 13.5, 7.0, 2.0, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.9 (*ipso*-$C_6H_4SO_2$), 137.9 (*ipso*-C_6H_4Me), 133.9 (=CH), 129.5 (*m*-C_6H_4Me), 127.1 (*o*-C_6H_4Me), 118.3 (=CH_2), 72.6 (CHO), 61.3 (CN), 53.7 (CHN), 33.2 (CH_2), 31.1 (CH_2), 29.3 (CH_2), 21.6 (Me); MS (CI, NH_3) m/z 311 [$(M + NH_4)^+$, 15], 294 (100), 276 (30), 138 (85); HRMS (CI, NH_3) m/z: $[M + H]^+$ calcd for $C_{15}H_{19}NO_3S$, 294.1164; found, 294.1164 and hydroxy aziridine *cis*-**62** (105 mg, 56%) as a colourless oil, R_F(3 : 7 Et_2O–hexane) 0.16; IR (film) 3502 (OH), 2955, 2928, 1598, 1437, 1399, 1318 (SO_2), 1156 (SO_2), 1091, 986 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.5, 2H, *m*-C_6H_4Me), 7.31 (br d, J = 8.5, 2H, *o*-C_6H_4Me), 5.87 (ddt, J = 17.0, 10.0, 7.0, 1H, =CH), 5.19–5.12 (m, 2H, =CH_2), 4.28 (br m, 1H, CHO), 3.44 (d, J = 3.0, 1H, CHN), 2.96 (dd, J = 15.0, 7.0, 1H, CH_AH_BCH=CH_2), 2.89 (dd, J = 15.0, 7.0, 1H, CH_AH_BCH=CH_2), 2.42 (s, 3H, Me), 2.04 (dd, J = 14.0, 8.5, 1H, CH), 1.91 (dt, J = 13.0, 8.0, 1H, CH), 1.67 (ddd, J = 14.0, 10.5, 8.0, 1H, CH), 1.26–1.12 (m, 2H, CH and OH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.0 (*ipso*-$C_6H_4SO_2$), 137.6 (*ipso*-C_6H_4Me), 133.3 (=CH), 129.6 (*m*-C_6H_4Me), 127.1 (*o*-C_6H_4Me), 118.6 (=CH_2), 73.0 (CHO), 60.1 (CN), 54.7 (CHN), 33.7 (CH_2), 29.9 (CH_2), 29.3 (CH_2), 21.6 (Me); MS (CI, NH_3) m/z 311 [$(M + NH_4)^+$, 20], 294 (100), 276 (30), 138 (35); HRMS (CI, NH_3) m/z: $[M + H]^+$ calcd for $C_{15}H_{19}NO_3S$, 294.1164; found, 294.1162.

5-(3-Butenyl)-6-[(4-methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]-hexan-2-ol *trans*-63 and *cis*-63. Using the general procedure, allylic alcohol **38** (355 mg, 2.6 mmol), chloramine-T trihydrate (796 mg, 2.8 mmol) and $PhMe_3NBr_3$ (97 mg, 0.3 mmol) in MeCN (12 mL) gave the crude product, which contained a 75 : 25 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**63** and *trans*-**63**. Purification by flash chromatography on silica with hexane–EtOAc (2 : 1) as eluent gave a 65 : 35 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridine *trans*-**63** and $TsNH_2$ (209 mg) as a white solid and hydroxy aziridine *cis*-**63** (418 mg, 53%) as a colourless oil, R_F(2 : 1 hexane–EtOAc) 0.1; IR (film) 3507 (OH), 2976, 2927, 1317 (SO_2), 1155 (SO_2), 1089, 998, 884, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5, 2H, *m*-C_6H_4Me), 7.33 (d, J = 8.5, 2H, *o*-C_6H_4Me), 5.83 (ddt, J = 17.0, 10.0, 6.0, 1H, CH=CH_2), 5.07 (app. dq, J = 17.0, 1.5, 1H, CH=CH_AH_B), 5.01 (app. dq, J = 10.0, 1.5, 1H, CH=CH_AH_B), 4.24 (td, J = 8.0, 2.5, 1H, CHO), 3.42 (d, J = 2.5, 1H, CHN), 2.47–2.39 (m, 1H, CH), 2.46 (s, 3H, Me), 2.46–2.20 (m, 3H, 3 × CH), 2.11 (dd, J = 14.0, 8.0, 1H, CH), 1.94 (dt, J = 13.0, 8.0, 1H, CH), 1.70 (ddd, J = 14.0, 10.5, 8.0, 1H, CH), 1.20 (ddt, J = 13.0, 10.5, 8.0, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.0 (*ipso*-$C_6H_4SO_2$), 137.9 (*ipso*-C_6H_4Me), 137.3 (=CH), 129.6 (*m*-C_6H_4Me), 127.1 (*o*-C_6H_4Me), 115.5 (=CH_2), 72.9 (CHO), 61.1 (CN), 55.4 (CHN), 30.8 (CH_2), 29.9 (CH_2), 29.4 (CH_2), 28.2 (CH_2), 21.6 (Me); MS (CI, NH_3) m/z 308 [$(M + H)^+$, 70], 290 (20), 152 (100); HRMS (CI, NH_3) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}NO_3S$, 308.1320; found, 308.1312. Further purification of the mixture of *trans*-**63** and $TsNH_2$ by partial recrystallisation from hexane–Et_2O followed by evaporation of the filtrate under reduced pressure gave hydroxy aziridine *trans*-**63** (118 mg, 15%) as a white solid, mp 80–82 °C, R_F(2 : 1 hexane–EtOAc) 0.1; IR (Nujol mull) 3520 (OH), 1456, 1378, 1308 (SO_2), 1152 (SO_2), 1090, 1021 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.30 (d, J = 8.0, 2H, *o*-C_6H_4Me), 5.90 (dddd, J = 17.0, 10.0, 6.5, 6.0, 1H, CH=CH_2), 5.11 (app. dq, J = 17.0, 2.0, 1H, CH=CH_AH_B), 5.04 (ddt, J = 10.0, 2.0, 1.0, 1H, CH=CH_AH_B), 4.12 (br t, J = 4.0, 1H, CHO), 3.31 (s, 1H, CHN), 2.53–2.28 (m, 3H, 3 × CH), 2.44 (s, 3H, Me), 2.01 (ddd, J = 13.5, 8.5, 1.5, 1H, CH), 1.93 (ddd, J = 13.5, 10.5, 8.0, 1H, CH), 1.69–1.50 (m, 3H, 3 × CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.8 (*ipso*-$C_6H_4SO_2$), 138.1 (*ipso*-C_6H_4Me), 137.9 (=CH), 129.5 (*m*-C_6H_4Me), 127.1 (*o*-C_6H_4Me), 115.4 (=CH_2), 72.6 (CHO), 62.1 (CN), 54.2 (CHN), 31.3 (CH_2), 31.1 (CH_2), 29.1 (CH_2), 27.6 (CH_2), 21.6 (Me); MS (CI, NH_3) m/z 325 [$(M + NH_4)^+$, 55], 308 (50), 189 (100), 119 (30); HRMS (CI, NH_3) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}NO_3S$, 308.1320; found, 308.1326.

7-(*tert*-Butylsulfonyl)-7-azabicyclo[4.1.0]heptan-2-ol *cis*-64. Using the general procedure, $PhMe_3NBr_3$ (150 mg, 0.4 mmol),

BusNClNa (928 mg, 4.8 mmol) and allylic alcohol **1** (392 mg, 4.0 mmol) in MeCN (20 mL) gave the crude product, which contained a 70 : 30 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**64** and *trans*-**64**. Purification by flash column chromatography on silica with chloroform–acetone (9 : 1) as eluent gave hydroxy aziridine *cis*-**64** (314 mg, 34%) as a colourless oil, R_F(9 : 1 chloroform–acetone) 0.1; IR (Nujol mull) 3508 (OH), 1293 (SO_2), 1120 (SO_2), 1065, 952; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11–4.04 (m, 1H, CHO), 3.23 (dd, J = 7.0, 4.0, 1H, CHN), 3.11 (ddd, J = 7.0, 5.0, 1.5, 1H, CHN), 1.94–1.76 (m, 3H, 2 × CH and OH), 1.68–1.42 (m, 3H, 3 × CH), 1.52 (s, 9H, CMe_3), 1.36–1.25 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 64.9 (CHO), 59.4 (SO_2C), 43.5 (CHN), 41.7 (CHN), 29.0 (CH_2), 24.2 (CMe_3), 21.7 (CH_2), 18.5 (CH_2); MS (CI, NH_3) m/z 251 [$(M + NH_4)^+$, 25], 234 (100), 114 (25); HRMS (CI, NH_3) m/z: [M + H]$^+$ calcd for $C_{10}H_{19}NO_3S$, 234.1164; found, 234.1166. Diagnostic signals for hydroxy aziridine *trans*-**64**: (400 MHz, $CDCl_3$) δ 3.06–3.03 (m, 1H, CHN) and 2.95 (d, J = 6.5, 1H, CHN).

7-(*tert*-Butylsulfonyl)-6-methyl-7-azabicyclo[4.1.0]heptan-2-ol *cis*-65. Using the general procedure, $PhMe_3NBr_3$ (113 mg, 0.3 mmol), BusNClNa (639 mg, 3.3 mmol) and allylic alcohol **28** (336 mg, 3.0 mmol) in MeCN (15 mL) gave the crude product, which contained a 90 : 10 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**65** and *trans*-**65**. Purification by flash chromatography on silica with petrol–Et_2O (1 : 1) as eluent gave a 90 : 10 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**65** and *trans*-**65** (601 mg, 81%) as a colourless oil. Further purification by flash chromatography on silica with CH_2Cl_2–hexane–acetone (18 : 1 : 1) as eluent gave hydroxy aziridine *cis*-**65** (508 mg, 68%) as a colourless oil, R_F(18 : 1 : 1 CH_2Cl_2–hexane–acetone) 0.1; IR (film) 3501 (OH), 2939, 2869, 1455, 1399, 1298 (SO_2), 1122 (SO_2), 1096, 1017, 935 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13–4.07 (br m, 1H, CHO), 3.19 (d, J = 4.0, 1H, CHN), 1.98–1.91 (m, 2H, CH and OH), 1.65 (s, 3H, Me), 1.65–1.49 (m, 4H, 4 × CH), 1.51 (s, 9H, CMe_3), 1.35–1.26 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 65.5 (CHO), 60.0 (CMe_3), 53.4 (CN), 49.3 (CHN), 30.7 (CH_2), 28.8 (CH_2), 24.2 (CMe_3), 20.9 (Me), 18.2 (CH_2); MS (CI, NH_3) m/z 248 [$(M + H)^+$, 45], 128 (100), 126 (30); HRMS (CI, NH_3) m/z: [M + H]$^+$ calcd for $C_{11}H_{21}NO_3S$, 248.1320; found, 248.1318. Diagnostic signals for hydroxy aziridine *trans*-**65**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03–3.98 (m, 1H, CHO), 2.93 (s, 1H, CHN).

6-(3-Butenyl)-7-(*tert*-butylsulfonyl)-7-azabicyclo[4.1.0]heptan-2-ol *cis*-66. $PhMe_3NBr_3$ (216 mg, 0.6 mmol) was added in one portion to a stirred suspension of BusNClNa (1.34 g, 6.9 mmol) and allylic alcohol **31** (875 mg, 5.8 mmol) in acetone (30 mL) at 0 °C under N_2. After stirring for 6 h at 0 °C, the resulting suspension was filtered through a silica plug, and washed with Et_2O. The filtrate was evaporated under reduced pressure to give the crude product, which contained an 80 : 20 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**66** and *trans*-**66**. Purification by flash chromatography on silica with petrol–Et_2O (6 : 4) as eluent gave an 80 : 20 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**66** and *trans*-**66** (1.06 g, 64%) as a white solid. Recrystallisation from Et_2O–hexane (1 : 1) gave hydroxy aziridine *cis*-**66** (828 mg, 50%) as a white solid, mp 66–68 °C; R_F(1 : 1 petrol–Et_2O) 0.2; IR (film) 3525 (OH), 1284 (SO_2), 1118 (SO_2), 1073, 984, 941, 907 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (dddd, J = 17.0, 10.0, 7.0, 6.0, 1H, CH=CH_2), 5.05 (app. dq, J = 17.0, 1.5, 1H, CH=CH_AH_B), 5.01 (br d, J = 10.0, 1H, CH=CH_AH_B), 4.03 (ddt, J = 8.5, 5.5, 3.5, 1H, CHO), 3.14 (d, J = 3.5, 1H, CHN), 2.39–2.31 (m, 1H, CH), 2.19–2.00 (m, 3H, 3 × CH), 1.88 (d, J = 5.5, OH), 1.84–1.74 (m, 2H, 2 × CH), 1.67–1.52 (m, 2H, 2 × CH), 1.51 (s, 9H, CMe_3), 1.51–1.39 (m, 1H, CH), 1.29–1.19 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 137.2 (=CH), 115.7 (=CH_2), 66.4 (CHO), 60.4 (SO_2C), 56.2 (CN), 49.8 (CHN), 33.0 (CH_2), 31.2 (CH_2), 28.4 (CH_2), 27.4 (CH_2), 24.3 (CMe_3), 19.4 (CH_2); MS (CI, NH_3) m/z 305 [$(M + NH_4)^+$, 20], 288, (100), 168 (65), 155 (30); HRMS (CI, NH_3) m/z: [M + H]$^+$ calcd for $C_{14}H_{25}NO_3S$, 288.1633; found, 288.1639. Diagnostic signal for hydroxy aziridine *trans*-**66**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (s, 1H, CHN).

6-(*tert*-Butylsulfonyl)-6-azabicyclo[3.1.0]hexan-2-ol *cis*-67. Using the general procedure, $PhMe_3NBr_3$ (161 mg, 0.4 mmol), BusNClNa (1.01 g, 5.2 mmol) and allylic alcohol **35** (365 mg, 4.3 mmol) in MeCN (22 mL) gave the crude product, which contained an 80 : 20 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**67** and *trans*-**67**. Purification by flash column chromatography on silica with petrol–Et_2O (1 : 4) as eluent gave an 80 : 20 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**67** and *trans*-**67** (493 mg, 52%) as a colourless oil. Further purification by flash column chromatography with petrol–EtOAc (1 : 1) as eluent gave hydroxy aziridine *cis*-**67** (401 mg, 42%) as a white solid, mp 81–84 °C; R_F(1 : 1 petrol–EtOAc) 0.2; IR (Nujol mull) 3498 (OH), 1287 (SO_2), 1121 (SO_2), 1078, 971, 889; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.41 (td, J = 8.0, 2.5, 1H, CHO), 3.36 (dd, J = 5.0, 2.5, 1H, CHN), 3.24 (dd, J = 5.0, 2.5, 1H, CHN), 2.09 (br s, 1H, OH), 2.09 (dd, J = 14.0, 8.0, 1H, CH), 1.98 (dt, J = 13.0, 8.0, 1H, CH), 1.76 (dddd, J = 14.0, 11.0, 8.0, 2.5, 1H, CH), 1.52 (s, 9H, CMe_3), 1.33 (ddt, J = 13.0, 11.0, 8.0, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 72.6 (CHO), 59.7 (SO_2C), 47.4 (CHN), 44.3 (CHN), 28.1 (CH_2), 25.5 (CH_2), 24.2 (CMe_3); MS (CI, NH_3) m/z 237 [$(M + NH_4)^+$, 100], 220 (65), 100 (40); HRMS (CI, NH_3) m/z: [M + H]$^+$ calcd for $C_9H_{17}NO_3S$, 220.1007; found, 220.1004. Diagnostic signals for hydroxy aziridine *trans*-**67**: (400 MHz, $CDCl_3$) δ 3.38 (d, J = 4.5, 1H, CHN) and 3.32 (d, J = 4.5, 1H, CHN).

6-(*tert*-Butylsulfonyl)-5-methyl-6-azabicyclo[3.1.0]hexan-2-ol *cis*-68. Using the general procedure, $PhMe_3NBr_3$ (38 mg, 0.1 mmol), BusNClNa (232 mg, 1.2 mmol) and allylic alcohol **36** (98 mg, 1.0 mmol) in MeCN (5 mL) gave the crude product, which contained a 95 : 5 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**68** and *trans*-**68**. Purification by flash column chromatography on silica with petrol–EtOAc (1 : 1) as eluent gave a 95 : 5 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**68** and *trans*-**68** (136 mg, 58%) as a colourless oil. Further purification by recrystallisation from hexane–Et_2O (1 : 1) gave hydroxy aziridine *cis*-**68** (120 mg, 51%) as a white solid, mp 115–118 °C; R_F(1 : 1 petrol–EtOAc) 0.2; IR (Nujol mull) 3479 (OH), 1283 (SO_2), 1119 (SO_2), 1084 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (td, J = 8.0, 2.5, 1H, CHO), 3.22 (d, J = 2.5, 1H, CHN), 2.14 (dd, J = 13.5, 8.0, 1H, CH), 2.12 (br s, 1H, OH), 1.92 (dt, J = 12.0, 8.0, 1H, CH), 1.73 (s, 3H, Me), 1.59 (ddd, J = 13.5, 11.0, 8.0, 1H, CH), 1.51 (s, 9H, CMe_3), 1.47–1.39 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 73.3 (CHO), 60.9 (SO_2C), 54.9 (CHN), 54.1

(CN), 32.9 (CH_2), 29.1 (CH_2), 24.2 (CMe_3), 15.9 (Me); MS (CI, NH_3) *m/z* 251 [$(M + NH_4)^+$, 15], 234 (15), 216 (60), 114 (100), 96 (30); HRMS (CI, NH_3) *m/z:* [$M + NH_4]^+$ calcd for $C_{10}H_{19}NO_3S$, 251.1429; found, 251.1433. Diagnostic signal for hydroxy aziridine *trans*-**68**: (400 MHz, $CDCl_3$) δ 3.20 (s, 1H, CHN).

5-(3-Butenyl)-6-(*tert*-butylsulfonyl)-6-azabicyclo[3.1.0]hexan-2-ol *cis*-69. $PhMe_3NBr_3$ (192 mg, 0.5 mmol) was added in one portion to a stirred suspension of BusNClNa (1.2 g, 6.2 mmol) and allylic alcohol **38** (711 mg, 5.1 mmol) in acetone (25 mL) at 0 °C under N_2. After stirring for 6 h at 0 °C, the resulting suspension was filtered through a silica plug, and washed with Et_2O. The filtrate was evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica with petrol–Et_2O (1 : 1) as eluent gave a mixture of hydroxy aziridine *cis*-**69**, *trans*-**69** and $TsNH_2$ (1.15 g). Recrystallisation from Et_2O–hexane (1 : 1) gave hydroxy aziridine *cis*-**69** (1.06 g, 75%) as a white solid, mp 70–72 °C; R_F(1 : 1 petrol–Et_2O) 0.1; IR (film) 3599 (OH), 2986, 2939, 1298 (SO_2), 1274, 1124 (SO_2) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddt, J = 17.0, 10.5, 6.0, 1H, C*H*=CH_2), 5.04 (app. dq, J = 17.0, 1.5, 1H, CH=CH_AH_B), 5.01 (br d, J = 10.5, 1H, CH=CH_AH_B), 4.42–4.36 (m, 1H, CHO), 3.22 (d, J = 2.0, 1H, CHN), 2.45–2.34 (m, 1H, CH), 2.21–2.10 (m, 4H, 4 × CH), 1.97 (dt, J = 12.5, 8.0, 1H, CH), 1.95 (br s, 1H, OH), 1.74 (ddd, J = 13.5, 10.5, 8.0, 1H, CH), 1.54–1.46 (m, 1H, CH), 1.52 (s, 9H, CMe_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 138.0 (=CH), 115.2 (=CH_2), 73.1 (CHO), 60.8 (CN), 56.7 (SO_2C), 54.7 (CHN), 31.0 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 28.8 (CH_2), 24.3 (CMe_3); MS (CI, NH_3) *m/z* 291 [$(M + NH_4)^+$, 35], 274 (30), 256 (75), 210 (25), 154 (100); HRMS (CI, NH_3) *m/z*: [$M + NH_4]^+$ calcd for $C_{13}H_{23}NO_3S$, 291.1742; found, 291.1742.

4-Methyl-*N*-(7-oxabicyclo[4.1.0]hept-2-yl)benzenesulfonamide *trans*-71. KHMDS (3.0 mL of a 0.5 M solution in toluene, 1.5 mmol) was added dropwise to a stirred solution of hydroxy aziridine *trans*-**2** (104 mg, 0.4 mmol) in THF (6 mL) at 0 °C under N_2. The resulting solution was stirred at 0 °C for 3 h then cooled to −78 °C. Saturated $NH_4Cl_{(aq)}$ (10 mL) was added and the resulting mixture was allowed to warm to rt. The layers were separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with petrol–Et_2O (3 : 7) as eluent gave epoxy sulfonamide *trans*-**71** (84 mg, 81%) as an off-white solid, mp 85–87 °C; R_F(3 : 7 petrol–Et_2O) 0.3; IR (CH_2Cl_2) 3431 (NH), 2943, 1643, 1599, 1447, 1327 (SO_2), 1161 (SO_2), 1089, 895, 816, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5, 2H, *m*-C_6H_4Me), 7.31 (d, J = 8.5, 2H, *o*-C_6H_4Me), 5.52 (d, J = 8.0, 1H, NH), 3.53 (app. q, J = 8.0, 1H, CHN), 3.10 (s, 1H, CHO), 2.98 (d, J = 3.5, 1H, CHO), 2.42 (s, 3H, Me), 1.92 (dt, J = 15.5, 5.5, 1H, CH), 1.73–1.58 (m, 2H, 2 × CH), 1.35–1.17 (m, 2H, 2 × CH), 1.10–1.02 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.6 (*ipso*-$C_6H_4SO_2$), 137.3 (*ipso*-C_6H_4Me), 129.8 (*m*-C_6H_4Me), 127.0 (*o*-C_6H_4Me), 54.7 (CHO), 52.4 (CHO), 48.8 (CHN), 27.1 (CH_2), 23.3 (CH_2), 21.5 (Me), 15.1 (CH_2); MS (CI, NH_3) *m/z* 285 [$(M + NH_4)^+$, 40], 268 (100), 189 (25), 98 (20); HRMS (CI, NH_3) *m/z*: [$M + H]^+$ calcd for $C_{13}H_{17}NO_3S$, 268.1007; found, 268.1006. Spectroscopic data consistent with those reported in the literature.[20]

4-Methyl-*N*-(6-oxabicyclo[3.1.0]hept-2-yl)benzenesulfonamide *trans*-72. KHMDS (4.0 mL of a 0.5 M solution in toluene, 2.0 mmol) was added dropwise to a stirred solution of hydroxy aziridine *trans*-**60** (126 mg, 0.5 mmol) in THF (8 mL) at 0 °C under N_2. The resulting solution was stirred at 0 °C for 3 h then cooled to −78 °C. Saturated $NH_4Cl_{(aq)}$ (10 mL) was added and the resulting mixture was allowed to warm to rt. The layers were separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with petrol–Et_2O (3 : 7) as eluent gave epoxy sulfonamide *trans*-**72** (93 mg, 74%) as an off-white solid, mp 93–95 °C; R_F(3 : 7 petrol–Et_2O) 0.3; IR (CH_2Cl_2) 3371 (NH), 3055, 2987, 1637, 1423, 1342 (SO_2), 1265, 1160 (SO_2), 896 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5, 2H, *m*-C_6H_4Me), 7.33 (d, J = 8.5, 2H, *o*-C_6H_4Me), 5.41 (br s, 1H, NH), 3.78 (t, J = 7.5, 1H, CHN), 3.45 (s, 1H, CHO), 3.32 (d, J = 1.5, 1H, CHO), 2.44 (s, 3H, Me), 1.94 (dd, J = 7.5, 5.5, 1H, CH), 1.73–1.53 (m, 2H, 2 × CH), 1.38 (dd, J = 8.0, 5.5, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.4 (*ipso*-$C_6H_4SO_2$), 137.2 (*ipso*-C_6H_4Me), 129.9 (*m*-C_6H_4Me), 127.0 (*o*-C_6H_4Me), 57.4 (CHO), 56.5 (CHO), 53.5 (CHN), 27.0 (CH_2), 24.7 (CH_2), 21.5 (Me); MS (CI, NH_3) *m/z* 271 [$(M + NH_4)^+$, 45], 254 (100), 236 (15), 189 (15); HRMS (CI, NH_3) *m/z*: [$M + H]^+$ calcd for $C_{12}H_{15}NO_3S$, 254.0851; found, 254.0853.

5-Allyl-6-[(4-methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]hexan-2-ol *cis*-62. Dess–Martin periodinane (1.35 g, 3.18 mmol) was added in one portion to a stirred solution of a 95 : 5 mixture (by ^1H NMR spectroscopy) of hydroxy aziridines *cis*-**62** and *trans*-**62** (778 mg, 2.65 mmol) in CH_2Cl_2 (10 mL) at rt under N_2. After stirring for 8 h, a solution of sodium thiosulfate pentahydrate (5.3 g) in 5% $NaHCO_{3(aq)}$ (10 mL) was added. After stirring for 15 min, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude keto aziridine **73**. Diagnostic signal for keto aziridine **73**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.26 (s, 1H, CHN). The crude keto aziridine **73** was dissolved in MeOH (40 mL) under N_2 and cooled to 0 °C. Then, $NaBH_4$ (301 mg, 7.95 mmol) was added and the resulting mixture was stirred at 0 °C for 3 h. After warming to rt, saturated $NH_4Cl_{(aq)}$ (3 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica with hexane–EtOAc (1 : 1) as eluent gave hydroxy aziridine *cis*-**62** (527 mg, 68%) as a colourless oil.

2-Methyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptan-2-ol *cis*-75 and 4-methyl-*N*-(6-methyl-7-oxabicyclo[4.1.0]hept-2-yl)benzenesulfonamide *trans*-79. Using the general procedure, allylic alcohol **39** (112 mg, 1.0 mmol), chloramine-T trihydrate (310 mg, 1.1 mmol) and $PhMe_3NBr_3$ (38 mg, 0.1 mmol) in MeCN (5 mL) gave the crude product, which contained a 75 : 25 mixture (by ^1H NMR spectroscopy) of hydroxy aziridines *cis*-**75** and *trans*-**75**. Purification by flash chromatography on silica with petrol–Et_2O (1 : 1) as eluent gave epoxysulfonamide *trans*-**79** (48 mg, 17%) as a white solid, mp 104–106 °C; R_F(1 : 1 petrol–Et_2O) 0.1; IR (Nujol mull) 3228 (NH), 1320 (SO_2), 1160 (SO_2), 1092 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, $J = 8.0$, 2H, *m*-C_6H_4Me), 7.28 (d, $J = 8.0$, 2H, *o*-C_6H_4Me), 5.29 (d, $J = 9.0$, 1H, NH), 3.70–3.64 (m, 1H, CHN), 2.81 (d, $J = 3.5$, 1H, CHO), 2.40 (s, 3H, Me), 1.80 (ddd, $J = 14.5, 7.5, 4.5$, 1H, CH), 1.59 (dt, $J = 14.5, 6.0$, 1H, CH), 1.45–1.33 (m, 3H, 3 × CH), 1.24 (s, 3H, Me), 1.24–1.15 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.2 (*ipso*-$C_6H_4SO_2$), 138.4 (*ipso*-C_6H_4Me), 129.6 (*m*-C_6H_4Me), 126.8 (*o*-C_6H_4Me), 61.3 (CHO), 60.9 (C(O)), 49.5 (CHN), 28.2 (CH_2), 27.3 (CH_2), 23.5 (Me), 21.5 (Me), 18.1 (CH_2); MS (CI, NH_3) *m*/*z* 299 [$(M + NH_4)^+$, 100], 282 (25), 95 (15); HRMS (CI, NH_3) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{14}H_{19}NO_3S$, 299.1429; found, 299.1438, and hydroxy aziridine *cis*-**75** (188 mg, 67%) as a white solid, mp 84–85 °C; R_F(1 : 1 petrol–Et_2O) 0.1; IR (CH_2Cl_2) 3563 (OH), 2948, 1326 (SO_2), 1162 (SO_2), 1091, 948 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, $J = 8.0$, 2H, *m*-C_6H_4Me), 7.36 (d, $J = 8.0$, 2H, *o*-C_6H_4Me), 3.23 (ddd, $J = 6.5, 4.5, 1.0$, 1H, CHN), 2.94 (d, $J = 6.5$, 1H, CHN), 2.45 (s, 3H, Me), 1.91 (s, 1H, OH), 1.84 (dt, $J = 15.0, 6.0$, 1H, CH), 1.76–1.67 (m, 1H, CH), 1.53–1.40 (m, 2H, 2 × CH), 1.33 (s, 3H, Me), 1.33–1.22 (m, 2H, 2 × CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.7 (*ipso*-$C_6H_4SO_2$), 134.8 (*ipso*-C_6H_4Me), 129.8 (*m*-C_6H_4Me), 127.8 (*o*-C_6H_4Me), 66.2 (CO), 48.7 (CHN), 42.8 (CHN), 36.0 (CH_2), 26.8 (Me), 22.1 (CH_2), 21.7 (Me), 17.0 (CH_2); MS (CI, NH_3) *m*/*z* 282 [$(M + H)^+$, 15], 264 (100), 126 (25); HRMS (CI, NH_3) *m*/*z*: $[M + H]^+$ calcd for $C_{14}H_{19}NO_3S$, 282.1164; found, 282.1167.

2-Butyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptan-2-ol *cis*-76 and *trans*-76. Using the general procedure, allylic alcohol **40** (154 mg, 1.0 mmol), chloramine-T trihydrate (310 mg, 1.1 mmol) and $PhMe_3NBr_3$ (38 mg, 0.1 mmol) in MeCN (5 mL) gave the crude product, which contained a 70 : 30 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**76** and *trans*-**76**. Purification by flash chromatography on silica with CH_2Cl_2–acetone (97 : 3) as eluent gave a 70 : 30 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**76** and *trans*-**76** (260 mg, 80%) as a colourless oil. Further purification by flash chromatography on silica with hexane–CH_2Cl_2–acetone (8 : 1 : 1) gave hydroxy aziridine *cis*-**76** as a colourless oil, R_F(8 : 1 : 1 hexane–CH_2Cl_2–acetone) 0.2; IR (film) 3521 (OH), 2937, 2871, 1598, 1455, 1403, 1324 (SO_2), 1159 (SO_2), 1091 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, $J = 8.5$, 2H, *m*-C_6H_4Me), 7.35 (br d, $J = 8.0$, 2H, *o*-C_6H_4Me), 3.23 (ddd, $J = 7.0, 3.5, 1.0$, 1H, CHN), 2.95 (d, $J = 7.0$, 1H, CHN), 2.44 (s, 3H, Me), 1.92 (dt, $J = 14.5, 5.0$, 1H, CH), 1.69–1.60 (m, 2H, CH_2), 1.58–1.53 (m, 2H, CH_2), 1.48–1.26 (m, 7H, 3 × CH_2 and OH), 1.20 (ddd, $J = 13.5, 11.0, 2.5$, 1H, CH), 0.91 (t, $J = 7.0$, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.7 (*ipso*-$C_6H_4SO_2$), 134.7 (*ipso*-C_6H_4Me), 129.8 (*m*-C_6H_4Me), 127.8 (*o*-C_6H_4Me), 67.4 (CO), 47.8 (CHN), 42.7 (CHN), 40.1 (CH_2), 34.3 (CH_2), 25.0 (CH_2), 23.1 (CH_2), 22.6 (CH_2), 21.7 (Me), 15.6 (CH_2), 14.1 (Me); MS (CI, NH_3) *m*/*z* 324 [$(M + H)^+$, 60], 306 (100), 168 (40); HRMS (CI, NH_3) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{15}NO_3S$, 324.1633; found, 324.1632. Diagnostic signals for hydroxy aziridine *trans*-**76**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70–3.64 (m, 1H, CHO), 2.76 (d, $J = 3.5$, 1H, CHN).

2-Allyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptan-2-ol *cis*-77 and *trans*-77. Using the general procedure, allylic alcohol **41** (138 mg, 1.0 mmol), chloramine-T trihydrate (310 mg, 1.1 mmol) and $PhMe_3NBr_3$ (38 mg, 0.1 mmol) in MeCN (5 mL) gave the crude product, which contained a 70 : 30 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**77** and *trans*-**77**. Purification by flash chromatography on silica with $CHCl_3$–acetone (98 : 2) as eluent gave a 70 : 30 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**77** and *trans*-**77** (142 mg, 46%) as a colourless oil. Hydroxy aziridines *cis*-**77** and *trans*-**77** could not be separated by flash chromatography on silica. Hydroxy aziridine *cis*-**77** was identified and characterised by independent synthesis (*vide infra*).

2-Isopropyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptan-2-ol *cis*-78 and *N*-(6-isopropyl-7-oxabicyclo[4.1.0]hept-2-yl)-4-methylbenzenesulfonamide *trans*-80. Using the general procedure, allylic alcohol **42** (119 mg, 0.9 mmol), chloramine-T trihydrate (262 mg, 0.9 mmol) and $PhMe_3NBr_3$ (32 mg, 0.1 mmol) in MeCN (4 mL) gave the crude product, which contained a 70 : 30 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**78** and *trans*-**78**. Purification by flash chromatography on silica with petrol–Et_2O (7 : 3) as eluent gave hydroxy aziridine *cis*-**78** (129 mg, 49%) as a white solid, mp 72–73 °C; R_F(7 : 3 petrol–Et_2O) 0.1; IR (Nujol mull) 3552 (OH), 1321 (SO_2), 1306, 1160 (SO_2), 1091, 963 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, $J = 8.5$, 2H, *m*-C_6H_4Me), 7.34 (br d, $J = 8.5$, 2H, *o*-C_6H_4Me), 3.25 (br dt, $J = 7.0, 1.5$, 1H, CHN), 2.98 (d, $J = 7.0$, 1H, CHN), 2.43 (s, 3H, Me), 2.15 (br s, 1H, OH), 1.98 (br d, $J = 14.5$, 1H, CH), 1.76 (septet, $J = 7.0$, 1H, C*H*Me_2), 1.59–1.51 (m, 1H, CH), 1.43–1.34 (m, 3H, 3 × CH), 1.20–1.11 (m, 1H, CH), 0.93 (d, $J = 7.0$, 3H, Me), 0.91 (d, $J = 7.0$, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.8 (*ipso*-$C_6H_4SO_2$), 134.6 (*ipso*-C_6H_4Me), 129.8 (*m*-C_6H_4Me), 127.8 (*o*-C_6H_4Me), 68.7 (CO), 47.0 (CHN), 42.6 (CHN), 37.1 (*C*HMe_2), 31.1 (CH_2), 23.1 (CH_2), 21.6 (Me), 16.6 (Me), 16.5 (Me), 14.1 (CH_2); MS (CI, NH_3) *m*/*z* 310 [$(M + H)^+$, 60], 292 (100), 154 (30); HRMS (CI, NH_3) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{23}NO_3S$, 310.1477; found, 310.1474 and epoxysulfonamide *trans*-**80** (52 mg, 20%) as a white solid, mp 108–110 °C; R_F(7 : 3 petrol–Et_2O) 0.1; IR (Nujol mull) 3226 (NH), 1326 (SO_2), 1157 (SO_2), 1091, 1010 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, $J = 8.0$, 2H, *m*-C_6H_4Me), 7.29 (d, $J = 8.0$, 2H, *o*-C_6H_4Me), 5.00 (d, $J = 9.5$, 1H, NH), 3.68–3.62 (m, 1H, CHN), 2.78 (d, $J = 3.0$, 1H, CHO), 2.42 (s, 3H, Me), 1.70–1.57 (m, 2H, CH), 1.50–1.22 (m, 4H, CH), 1.19–1.09 (m, 1H, CH), 0.87 (d, $J = 7.0$, 3H, Me), 0.84 (d, $J = 7.0$, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.3 (*ipso*-$C_6H_4SO_2$), 138.5 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 126.9 (*o*-C_6H_4Me), 67.6 (C(O)), 59.8 (CHO), 50.3 (CHN), 34.9 (*C*HMe_2), 27.5 (CH_2), 22.8 (CH_2), 21.5 (Me), 19.1 (CH_2), 17.9 (Me), 17.1 (Me); MS (CI, NH_3) *m*/*z* 310 [$(M + H)^+$, 100], 292 (20), 154 (25), 139 (20); HRMS (CI, NH_3) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{23}NO_3S$, 310.1477; found, 310.1476.

2-Allyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptan-2-ol *cis*-77. Dess–Martin periodinane (343 mg, 0.8 mmol) was added in one portion to a stirred solution of a 60 : 40 mixture (by ^{1}H NMR spectroscopy) of hydroxy aziridines *cis*-**2** and *trans*-**2** (180 mg, 0.7 mmol) in CH_2Cl_2 (10 mL) at rt under N_2. After stirring for 45 min, Et_2O (10 mL) and a solution of sodium thiosulfate pentahydrate (1.34 g) in 5% $NaHCO_{3(aq)}$ (15 mL) were added. After stirring for 15 min, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude keto aziridine **81**. Diagnostic signals for keto aziridine **81**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.46 (dtd, $J = 7.0, 2.0, 1.0$, 1H, CHN), 3.15 (d. $J = 7.0$, 1H, CHN). The

crude keto aziridine **81** was dissolved in THF (1.5 mL) and added dropwise *via* cannula to a stirred solution of allyl magnesium chloride (0.7 mL, 1.4 mmol) in THF (0.5 mL) at −78 °C under N_2. The reaction mixture was allowed to warm to 0 °C over 15 min, then stirred at 0 °C for 10 min. Saturated $NH_4Cl_{(aq)}$ (5 mL) was added, and the layers separated. The aqueous layer was extracted with Et_2O (3 × 5 mL) and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica with hexane–EtOAc–CH_2Cl_2 (16 : 3 : 1) as eluent gave hydroxy aziridine *cis*-**77** (65 mg, 31%) as a colourless oil, R_F(16 : 3 : 1 hexane–EtOAc–CH_2Cl_2) 0.1; IR (film) 3524 (OH), 2943, 1403, 1323 (SO_2), 1159 (SO_2), 1091, 979 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5, 2H, *m*-C_6H_4Me), 7.34 (br d, J = 8.5, 2H, *o*-C_6H_4Me), 5.83 (dddd, J = 17.0, 10.0, 7.5, 7.0, 1H, =CH), 5.16 (ddt, J = 10.0, 2.0, 1.0, 1H, =CH_AH_B), 5.13 (ddt, J = 17.0, 2.0, 1.5, 1H, =CH_AH_B), 3.22 (ddd, J = 7.0, 4.0, 1.0, 1H, CHN), 2.99 (d, J = 7.0, 1H, CHN), 2.45 (s, 3H, Me), 2.38 (br dd, J = 14.0, 7.0, 1H, CH_AH_BCH=CH_2), 2.29 (br dd, J = 14.0, 7.5, 1H, CH_AH_BCH=CH_2), 2.04 (s, 1H, OH), 1.92 (br dt, J = 15.0, 4.5, 1H, CH), 1.65 (dddd, J = 15.0, 9.5, 6.0, 4.0, 1H, CH), 1.49–1.30 (m, 3H, 3 × CH), 1.25–1.17 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.8 (*ipso*-$C_6H_4SO_2$), 134.6 (*ipso*-C_6H_4Me), 132.7 (=CH), 129.8 (*m*-C_6H_4Me), 127.9 (*o*-C_6H_4Me), 119.0 (=CH_2), 67.1 (CO), 47.0 (CHN), 44.7 (CH_2), 42.6 (CHN), 34.6 (CH_2), 22.5 (CH_2), 21.7 (Me) 15.5 (CH_2); MS (CI, NH_3) m/z 325 [(M + NH_4)$^+$, 25], 308 (75), 290 (100); HRMS (CI, NH_3) m/z: [M + H]$^+$ calcd for $C_{16}H_{21}NO_3S$, 308.1320; found, 308.1319.

4-Methyl-*N*-(5-methyl-6-oxabicyclo[3.1.0]hex-2-yl)benzenesulfonamide *cis*-83. Using the general procedure, allylic alcohol **43** (98 mg, 1.0 mmol), chloramine-T trihydrate (310 mg, 1.1 mmol) and $PhMe_3NBr_3$ (38 mg, 0.1 mmol) in MeCN (5 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (1 : 1) as eluent gave epoxy sulfonamide *cis*-**83** (122 mg, 46%) as a colourless oil, R_F(1 : 1 petrol–Et_2O) 0.2; IR (film) 3262 (NH), 2956, 2929, 1444, 1424, 1324 (SO_2), 1160 (SO_2), 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.5, 2H, *m*-C_6H_4Me), 7.30 (br d, J = 8.5, 2H, *o*-C_6H_4Me), 4.75 (d, J = 10.0, 1H, NH), 3.86–3.79 (m, 1H, CHN), 3.04 (d, J = 1.0, 1H, CHO), 2.43 (s, 3H, Me), 1.89 (dd, J = 14.0, 8.5, 1H, CH), 1.74 (dt, J = 13.0, 8.5, 1H, CH), 1.52 (ddd, J = 14.0, 10.5, 8.5, 1H, CH), 1.17 (s, 3H, Me), 1.12 (ddt, J = 13.0, 10.5, 8.5, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.5 (*ipso*-$C_6H_4SO_2$), 137.9 (*ipso*-C_6H_4Me), 129.8 (*m*-C_6H_4Me), 127.0 (*o*-C_6H_4Me), 63.81 (CO), 63.77 (CHO), 55.3 (CHN), 30.2 (CH_2), 27.2 (CH_2), 21.6 (Me), 17.6 (Me); MS (CI, NH_3) m/z 285 [(M + NH_4)$^+$, 60], 268 (100), 250 (65), 112 (30), 96 (35); HRMS (CI, NH_3) m/z: [M + NH_4]$^+$ calcd for $C_{13}H_{17}NO_3S$, 285.1273; found, 285.1277.

Crystal structure determination of 4-methyl-*N*-(5-methyl-6-oxabicyclo[3.1.0]hex-2-yl)benzenesulfonamide *cis*-83.

Crystal data. $C_{13}H_{17}NO_3S$, M = 267.34, orthorhombic, a = 9.8353(6), b = 17.4256(13), c = 31.038 (2) Å, U = 5319.5(6) Å^3, T = 110(2) K, space group $P2_12_12_1$, Z = 16, μ(Mo-Kα) = 0.243 mm^{-1}, 41 651 reflections measured, 4564 unique (R_{int} = 0.0470) which were used in all calculations. The final $R1$ was 0.0600 ($I > 2\sigma_I$) and $wR2$ was 0.1674 (all data). CCDC reference number 692182.

***N*-(5-Butyl-6-oxabicyclo[3.1.0]hex-2-yl)-4-methylbenzenesulfonamide *cis*-85.** Using the general procedure, allylic alcohol **44** (140 mg, 1.0 mmol), chloramine-T trihydrate (310 mg, 1.1 mmol) and $PhMe_3NBr_3$ (38 mg, 0.1 mmol) in MeCN (5 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (1 : 1) as eluent gave epoxy sulfonamide *cis*-**85** (151 mg, 49%) as a white solid, mp 94–96 °C; R_F(1 : 1 petrol–Et_2O) 0.2; IR (Nujol mull) 3197 (NH), 1326 (SO_2), 1163 (SO_2), 1094, 817 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.29 (d, J = 8.0, 2H, *o*-C_6H_4Me), 5.02 (d, J = 9.0, 1H, NH), 3.82–3.75 (m, 1H, CHN), 3.07 (d, J = 1.0, 1H, CHO), 2.42 (s, 3H, Me), 1.89 (dd, J = 14.0, 8.0, 1H, CH), 1.74–1.47 (m, 4H, 4 × CH), 1.30–1.26 (m, 4H, 4 × CH), 1.16–1.06 (m, 1H, CH), 0.86 (t, J = 7.0, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.4 (*ipso*-$C_6H_4SO_2$), 138.0 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 127.0 (*o*-C_6H_4Me), 66.9 (CO), 62.9 (CHO), 55.0 (CHN), 31.1 (CH_2), 28.1 (CH_2), 27.2 (CH_2), 26.7 (CH_2), 22.6 (CH_2), 21.5 (Me), 13.9 (Me); MS (CI, NH_3) m/z 327 [(M + NH_4)$^+$, 30], 310 (100), 292 (70), 154 (30), 138 (35), 106 (20); HRMS (CI, NH_3) m/z: [M + H]$^+$ calcd for $C_{16}H_{23}NO_3S$, 310.1477; found, 310.1476.

***N*-(5-Allyl-6-oxabicyclo[3.1.0]hex-2-yl)-4-methylbenzenesulfonamide *cis*-87.** Using the general procedure, allylic alcohol **26** (124 mg, 1.0 mmol), chloramine-T trihydrate (310 mg, 1.1 mmol) and $PhMe_3NBr_3$ (38 mg, 0.1 mmol) in MeCN (5 mL) gave the crude product. Purification by flash chromatography on silica with $CHCl_3$–acetone (95 : 5) as eluent gave epoxy sulfonamide *cis*-**87** (158 mg, 54%) as a colourless oil, R_F(9 : 1 $CHCl_3$–acetone) 0.6; IR (film) 3259 (NH), 2978, 2953, 1434, 1326 (SO_2), 1159 (SO_2), 1093, 1048, 918, 817 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0, 2H, *m*-C_6H_4Me), 7.30 (d, J = 8.0, 2H, *o*-C_6H_4Me), 5.72–5.62 (m, 1H, =CH), 5.10–5.05 (m, 2H, =CH_2), 4.74 (d, J = 10.0, 1H, NH), 3.84–3.77 (m, 1H, CHN), 3.10 (d, J = 1.0, 1H, CHO), 2.431 (ddt, J = 15.0, 7.0, 1.0, 1H, CH_AH_BCH=CH_2), 2.428 (s, 3H, Me), 2.38 (ddt, J = 15.0, 7.5, 1.0, 1H, CH_AH_BCH=CH_2), 1.89 (dd, J = 14.0, 8.0, 1H, CH), 1.74 (dt, J = 13.0, 8.0, 1H, CH), 1.58–1.51 (m, 1H, CH), 1.16–1.06 (m, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.5 (*ipso*-$C_6H_4SO_2$), 137.9 (*ipso*-C_6H_4Me), 132.4 (=CH), 129.8 (*m*-C_6H_4Me), 127.0 (*o*-C_6H_4Me), 118.3 (=CH_2), 66.0 (CO), 62.3 (CHO), 55.0 (CHN), 36.0 (CH_2), 28.1 (CH_2), 26.8 (CH_2), 21.5 (Me); MS (CI, NH_3) m/z 311 [(M + NH_4)$^+$, 45], 294 (100), 276 (55), 138 (25), 122 (20); HRMS (CI, NH_3) m/z: [M + H]$^+$ calcd for $C_{15}H_{19}NO_3S$, 294.1164; found, 294.1163.

$PhMe_3NBr_3$ (24 mg, 0.1 mmol) was added in one portion to a stirred suspension of chloramine-T trihydrate (200 mg, 0.7 mmol) and allylic alcohol **26** (80 mg, 0.6 mmol) in MeCN (3 mL) at rt under N_2. After stirring at rt for 36 h, the resulting suspension was filtered through a silica plug and washed well with Et_2O. The filtrate was evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica with $CHCl_3$–acetone (95 : 5) as eluent gave epoxy sulfonamide *cis*-**87** (182 mg, 97%) as a colourless oil.

2,6-Dimethyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]-heptan-2-ol *cis*-91. Using the general procedure, allylic alcohol **45** (126 mg, 1.0 mmol), chloramine-T trihydrate (310 mg, 1.1 mmol) and $PhMe_3NBr_3$ (38 mg, 0.1 mmol) in MeCN (5 mL) gave the crude product. Purification by flash chromatography on silica with CH_2Cl_2–acetone (97 : 3) as eluent gave hydroxy aziridine *cis*-**91**

(206 mg, 70%) as a colourless oil, R_F(97 : 3 CH_2Cl_2–acetone) 0.17; IR (film) 3525 (OH), 2936, 2872, 1661, 1599, 1319 (SO_2), 1290, 1156 (SO_2), 1091, 1033 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.0$, 2H, *m*-C_6H_4Me), 7.33 (br d, $J = 8.0$, 2H, *o*-C_6H_4Me), 3.07 (s, 1H, CHN), 2.42 (s, 3H, Me), 2.08 (dt, $J = 14.5$, 3.5, 1H, CH), 1.75 (s, 3H, Me), 1.61 (s, 1H, OH), 1.49–1.42 (m, 2H, 2 × CH), 1.40–1.08 (m, 2H, 2 × CH), 1.30 (s, 3H, Me), 1.11 (ddd, $J =$ 14.5, 11.5, 3.0, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.2 (*ipso*-$C_6H_4SO_2$), 137.4 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 127.4 (*o*-C_6H_4Me), 66.3 (C(O)), 56.3 (CHN), 54.4 (C(N)), 36.6 (CH_2), 31.6 (CH_2), 27.9 (Me), 21.6 (Me), 20.1 (Me), 16.4 (CH_2); MS (CI, NH_3) *m*/*z* 296 [(M + H)$^+$, 100], 278 (25), 140 (40), 125 (15); HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{15}H_{21}NO_3S$, 296.1320; found, 296.1316.

2-Butyl-6-methyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]-heptan-2-ol *cis*-92. Using the general procedure, allylic alcohol **46** (168 mg, 1.0 mmol), chloramine-T trihydrate (310 mg, 1.1 mmol) and $PhMe_3NBr_3$ (38 mg, 0.1 mmol) in MeCN (5 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (1 : 1) as eluent gave hydroxy aziridine *cis*-**92** (303 mg, 90%) as a colourless oil, R_F(6 : 4 petrol–Et_2O) 0.31; IR (film) 3563 (OH), 2935, 2871, 1454, 1406, 1322 (SO_2), 1187, 1156 (SO_2), 1091, 1020, 963 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.5$, 2H, *m*-C_6H_4Me), 7.34 (br d, $J = 8.5$, 2H, *o*-C_6H_4Me), 3.09 (s, 1H, CHN), 2.43 (s, 3H, Me), 2.14–2.10 (m, 1H, CH), 1.76 (s, 3H, Me), 1.66 (s, 1H, OH), 1.57–1.53 (m, 2H, 2 × CH), 1.44–1.33 (m, 8H, 8 × CH), 1.15–1.08 (m, 1H, CH), 0.93 (t, $J = 7.0$, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.2 (*ipso*-$C_6H_4SO_2$), 137.5 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 127.4 (*o*-C_6H_4Me), 67.9 (CO), 55.7 (CHN), 54.3 (CN), 40.9 (CH_2), 34.7 (CH_2), 31.9 (CH_2), 25.1 (CH_2), 23.2 (CH_2), 21.6 (Me), 20.0 (Me), 15.7 (CH_2), 14.0 (Me); MS (CI, NH_3) *m*/*z* 338 [(M + H)$^+$, 100], 320 (70), 182 (55), 167 (65); HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{18}H_{27}NO_3S$, 338.1790; found, 338.1792.

6-Butyl-2-methyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]-heptan-2-ol *cis*-93. Using the general procedure, allylic alcohol **47** (890 mg, 5.3 mmol), chloramine-T trihydrate (1.64 g, 5.8 mmol) and $PhMe_3NBr_3$ (199 mg, 0.5 mmol) in MeCN (25 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O–Et_3N (50 : 50 : 1) as eluent gave hydroxy aziridine *cis*-**93** (1.31 g, 73%) as an off-white solid, mp 66–67 °C, R_F(1 : 1 petrol–Et_2O) 0.21; IR (film) 3566 (OH), 2937, 2871, 1456, 1407, 1381, 1322 (SO_2), 1156 (SO_2), 1090, 1004, 956, 862 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.5$, 2H, *m*-C_6H_4Me), 7.32 (d, $J = 8.5$, 2H, *o*-C_6H_4Me), 3.04 (s, 1H, CHN), 2.42 (s, 3H, Me), 2.13–2.00 (m, 2H, CH_2), 1.95 (dt, $J = 14.5$, 5.5, 1H, CH), 1.63 (ddd, $J = 14.5$, 9.0, 5.5, 1H, CH), 1.59–1.52 (m, 2H, CH_2), 1.45–1.31 (m, 5H, 5 × CH), 1.29 (s, 3H, Me), 1.18–1.11 (m, 1H, CH), 0.93 (t, $J = 7.0$, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.1 (*ipso*-$C_6H_4SO_2$), 137.6 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 127.4 (*o*-C_6H_4Me), 69.9 (CO), 58.8 (CN), 56.0 (CHN), 36.4 (CH_2), 32.9 (CH_2), 29.2 (CH_2), 28.1 (CH_2), 27.2 (Me), 22.5 (CH_2), 21.6 (Me), 17.0 (CH_2), 14.0 (Me); MS (CI, NH_3) *m*/*z* 338 [(M + H)$^+$, 85], 320 (25), 182 (100), 167 (35), 149 (20); HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{18}H_{27}NO_3S$, 338.1790; found, 338.1791.

Crystal structure determination of 6-butyl-2-methyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptan-2-ol *cis*-93.

Crystal data. $C_{18}H_{27}NO_3S$, $M = 337.47$, monoclinic, $a =$ 12.940(3), $b = 12.042(2)$, $c = 11.540(2)$ Å, $\beta = 93.062(4)°$, $U =$ 1795.8(6) Å^3, $T = 100(2)$ K, space group $P2_1/c$, $Z = 4$, μ(Mo-Kα) = 0.194 mm^{-1}, 11 428 reflections measured, 4098 unique ($R_{int} = 0.0518$) which were used in all calculations. The final $R1$ was 0.0440 ($I > 2\sigma_I$) and $wR2$ was 0.1258 (all data). CCDC reference number 692183.†

6-Allyl-6-[(4-methylphenyl)sulfonyl]-2-butyl-7-azabicyclo[4.1.0]-heptan-2-ol *cis*-94. Using the general procedure, allylic alcohol **48** (194 mg, 1.0 mmol), chloramine-T trihydrate (310 mg, 1.1 mmol) and $PhMe_3NBr_3$ (38 mg, 0.1 mmol) in MeCN (5 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (7 : 3) as eluent gave hydroxy aziridine *cis*-**94** (194 mg, 53%) as a colourless oil, R_F(7 : 3 petrol–Et_2O) 0.21; IR (film) 3563 (OH), 2935, 2870, 1441, 1405, 1326 (SO_2), 1156 (SO_2), 1090, 991, 920, 865 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.5$, 2H, *m*-C_6H_4Me), 7.33 (br d, $J =$ 8.5, 2H, *o*-C_6H_4Me), 5.83 (ddt, $J = 17.0$, 10.0, 7.0, 1H, =CH), 5.17 (ddt, $J = 17.0$, 2.0, 1.0, 1H, =CH_AH_B), 5.15 (ddt, $J = 10.0$, 2.0, 1.0, 1H, =CH_AH_B), 3.11 (s, 1H, CHN), 2.84 (app. d, $J =$ 7.0, 2H, CH_2CH=CH_2), 2.42 (s, 3H, Me), 1.96 (dt, $J = 14.5$, 4.5, 1H, CH), 1.63–1.52 (m, 4H, 3 × CH and OH), 1.43–1.25 (m, 7H, 7 × CH), 1.15–1.08 (m, 1H, CH), 0.92 (t, $J = 6.5$, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.3 (*ipso*-$C_6H_4SO_2$), 137.4 (*ipso*-C_6H_4Me), 133.8 (=CH), 129.7 (*m*-C_6H_4Me), 127.4 (*o*-C_6H_4Me), 118.7 (=CH_2), 68.1 (CO), 57.0 (CN), 54.9 (CHN), 40.4 (CH_2), 38.0 (CH_2), 34.4 (CH_2), 28.2 (CH_2), 25.1 (CH_2), 23.1 (CH_2), 21.6 (Me), 15.9 (CH_2), 14.0 (Me); MS (CI, NH_3) *m*/*z* 364 [(M + H)$^+$, 70], 346 (35), 208 (100), 193 (20); HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{20}H_{29}NO_3S$, 364.1946; found, 364.1944.

2-Butyl-6-isopropyl-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo-[4.1.0]heptan-2-ol *cis*-95. Using the general procedure, allylic alcohol **49** (120 mg, 0.6 mmol), chloramine-T trihydrate (189 mg, 0.7 mmol) and $PhMe_3NBr_3$ (23 mg, 0.1 mmol) in MeCN (3 mL) gave the crude product, which contained a 65 : 35 mixture (by ^1H NMR spectroscopy) of hydroxy aziridines *cis*-**95** and *trans*-**95**. Purification by flash chromatography on silica with petrol–Et_2O (7 : 3) as eluent gave hydroxy aziridine *cis*-**95** (51 mg, 23%) as a colourless oil, R_F(7 : 3 petrol–Et_2O) 0.3; IR (film) 3563 (OH), 2956, 2935, 2872, 1325 (SO_2), 1155 (SO_2), 1090, 979, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, $J = 8.0$, 2H, *m*-C_6H_4Me), 7.32 (d, $J = 8.0$, 2H, *o*-C_6H_4Me), 3.00 (s, 1H, CHN), 2.44 (septet, $J =$ 7.0, 1H, CHMe$_2$), 2.42 (s, 3H, Me), 1.95 (dt, $J = 14.5$, 5.0, 1H, CH), 1.61–1.50 (m, 4H, 4 × CH), 1.41–1.25 (m, 7H, 6 × CH and OH), 1.21 (d, $J = 7.0$, 1H, CHMe_AMe$_B$), 1.17–1.09 (m, 1H, CH), 1.03 (d, $J = 7.0$, 3H, CHMe$_A$$Me_B$), 0.91 (t, $J = 7.0$, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.1 (*ipso*-$C_6H_4SO_2$), 137.7 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 127.4 (*o*-C_6H_4Me), 68.3 (CO), 64.0 (CN), 55.5 (CHN), 40.0 (CH_2), 34.2 (CH_2), 31.3 (*C*HMe$_2$), 25.1 (CH_2), 23.1 (CH_2), 22.8 (CH_2), 21.6 (Me), 20.9 (Me), 18.3 (Me), 16.1 (CH_2), 14.0 (Me); MS (CI, NH_3) *m*/*z* 366 [(M + H)$^+$, 85], 348 (40), 210 (100), 195 (30); HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{20}H_{31}NO_3S$, 348.2103; found, 348.2096.

2,5-Dimethyl-6-[(4-methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]-hexan-2-ol *cis*-96. Using the general procedure, allylic alcohol **50**

(90 mg, 0.8 mmol), chloramine-T trihydrate (249 mg, 0.9 mmol) and $PhMe_3NBr_3$ (30 mg, 0.1 mmol) in MeCN (4 mL) gave the crude product. Purification by flash chromatography on silica with $CHCl_3$–acetone (95 : 5) as eluent gave hydroxy aziridine *cis*-**96** (174 mg, 77%) as a colourless oil, R_F(95 : 5 $CHCl_3$–acetone) 0.40; IR (film) 3498 (OH), 2969, 2933, 1453, 1403, 1381, 1305 (SO_2), 1158 (SO_2), 1090, 1069, 1021, 873, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.5$, 2H, *m*-C_6H_4Me), 7.32 (br d, $J = 8.5$, 2H, *o*-C_6H_4Me), 3.19 (s, 1H, CHN), 2.43 (s, 3H, Me), 2.16–2.11 (m, 1H, CH), 1.82 (s, 3H, Me), 1.62–1.51 (m, 3H, 2 × CH and OH), 1.43–1.28 (m, 1H, CH), 1.24 (s, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.1 (*ipso*-$C_6H_4SO_2$), 137.7 (*ipso*-C_6H_4Me), 129.7 (*m*-C_6H_4Me), 127.1 (*o*-C_6H_4Me), 78.1 (CO), 59.4 (CHN), 57.4 (CN), 36.4 (CH_2), 33.4 (CH_2), 23.4 (Me), 21.6 (Me), 15.4 (Me); MS (CI, NH_3) *m*/*z* 282 [(M + H)$^+$, 100], 264 (75), 126 (90), 110 (15), 82 (15); HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{14}H_{19}NO_3S$, 282.1164; found, 282.1162.

2-Butyl-5-methyl-6-[(4-methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]-hexan-2-ol *cis*-97. Using the general procedure, allylic alcohol **51** (154 mg, 1.0 mmol), chloramine-T trihydrate (310 mg, 1.1 mmol) and $PhMe_3NBr_3$ (38 mg, 0.1 mmol) in MeCN (5 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (1 : 1) as eluent gave hydroxy aziridine *cis*-**97** (242 mg, 75%) as a colourless oil, R_F(3 : 7 petrol–Et_2O) 0.38; IR (film) 3511 (OH), 2956, 2934, 2871, 1454, 1403, 1317 (SO_2), 1157 (SO_2), 1090, 1010, 933, 872, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, $J = 8.5$, 2H, *m*-C_6H_4Me), 7.33 (d, $J = 8.5$, 2H, *o*-C_6H_4Me), 3.24 (s, 1H, CHN), 2.43 (s, 3H, Me), 2.14 (dd, $J =$ 13.5 and 8.5, 1H, CH), 1.83 (s, 3H, Me), 1.69 (dd, $J = 13.5$, 8.5, 1H, CH), 1.63–1.45 (m, 3H, 3 × CH), 1.39–1.25 (m, 5H, 5 × CH), 1.12 (s, 1H, OH), 0.92 (t, $J = 7.5$, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.9 (*ipso*-$C_6H_4SO_2$), 137.7 (*ipso*-C_6H_4Me), 129.6 (*m*-C_6H_4Me), 127.0 (*o*-C_6H_4Me), 80.3 (CO), 59.0 (CHN), 57.6 (CN), 36.6 (CH_2), 34.6 (CH_2), 33.7 (CH_2), 25.3 (CH_2), 23.1 (CH_2), 21.5 (Me), 15.2 (Me), 13.9 (Me); MS (CI, NH_3) *m*/*z* 341 [(M + NH_4)$^+$, 35], 324 (100), 306 (85), 189 (35), 168 (20), 153 (45); HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{25}NO_3S$, 324.1633; found, 324.1643.

5-Allyl-6-[(4-methylphenyl)sulfonyl]-2-butyl-6-azabicyclo[3.1.0]-hexan-2-ol *cis*-98. Using the general procedure, allylic alcohol **52** (116 mg, 0.6 mmol), chloramine-T trihydrate (198 mg, 0.7 mmol) and $PhMe_3NBr_3$ (24 mg, 0.1 mmol) in MeCN (3 mL) gave the crude product. Purification by flash chromatography on silica with petrol–Et_2O (1 : 1) as eluent gave hydroxy aziridine *cis*-**98** (72 mg, 32%) as a colourless oil, R_F(1 : 1 petrol–Et_2O) 0.24; IR (film) 3520 (OH), 2956, 2933, 1320 (SO_2), 1157 (SO_2), 1091, 933 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.5$, 2H, *m*-C_6H_4Me), 7.32 (br d, $J = 8.5$, 2H, *o*-C_6H_4Me), 5.86 (ddt, $J =$ 17.0, 10.0, 7.0, 1H, =CH), 5.21–5.13 (m, 2H, =CH_2), 3.27 (s, 1H, CHN), 2.96 (br dd, $J = 14.5$, 7.0, 1H, $CH_AH_BCH{=}CH_2$), 2.91 (br dd, $J = 14.5$, 7.0, 1H, $CH_AH_BCH{=}CH_2$), 2.41 (s, 3H, Me), 2.02 (dd, $J = 13.0$, 8.5, 1H, CH), 1.70–1.62 (m, 2H, 2 × CH), 1.54–1.17 (m, 8H, 7 × CH and OH), 0.90 (t, $J = 7.0$, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.1 (*ipso*-$C_6H_4SO_2$), 137.6 (*ipso*-C_6H_4Me), 133.3 (=CH), 129.7 (*m*-C_6H_4Me), 127.0 (*o*-C_6H_4Me), 118.7 (=CH_2), 80.3 (CO), 60.5 (CHN), 58.0 (CN), 36.3 (CH_2), 34.3 (CH_2), 33.7 (CH_2), 30.2 (CH_2), 25.3 (CH_2), 23.1 (CH_2), 21.5 (Me), 13.9 (Me); MS (CI, NH_3) *m*/*z* 350 [(M + H)$^+$, 100], 332 (100), 294 (35), 194 (55), 179 (20); HRMS (CI, NH_3) *m*/*z*: [M + H]$^+$ calcd for $C_{19}H_{27}NO_3S$, 350.1790; found, 350.1791.

2-Butyl-5-methyl-6-[(4-methylphenyl)sulfonyl]-6-azabicyclo[3.1.0]-hexan-2-ol *cis*-97. Dess–Martin periodinane (952 mg, 2.2 mmol) was added in one portion to a stirred solution of an 80 : 20 mixture (by ^1H NMR spectroscopy) of hydroxy aziridines *cis*-**61** and *trans*-**61** (500 mg, 1.9 mmol) in CH_2Cl_2 (25 mL) at rt under N_2. After stirring for 45 min, Et_2O (25 mL) and a solution of sodium thiosulfate pentahydrate (3.92 g) in 5% $NaHCO_{3(aq)}$ (30 mL) were added. After stirring for 15 min, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude keto aziridine **99**. The crude keto aziridine **99** was dissolved in THF (2.5 mL) and added dropwise *via* cannula to a stirred solution of butyl magnesium bromide (1.9 mL of a 2.00 M solution in THF, 3.7 mmol) in THF (10 mL) at −78 °C under N_2. The resulting solution was allowed to warm to 0 °C over 15 min, and stirred at 0 °C for 10 min. Saturated $NH_4Cl_{(aq)}$ (15 mL) was added and the layers separated. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica with petrol–Et_2O (3 : 7) as eluent gave hydroxy aziridine *cis*-**97** (414 mg, 68%) as a colourless oil.

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